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# The Journal *of the* SOCIETY OF DYERS AND COLOURISTS

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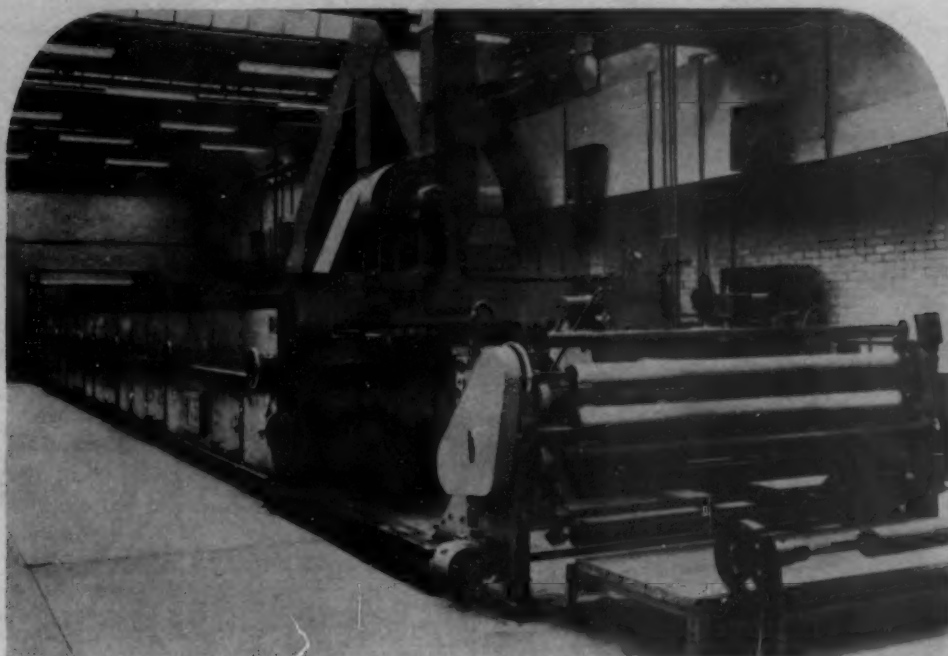
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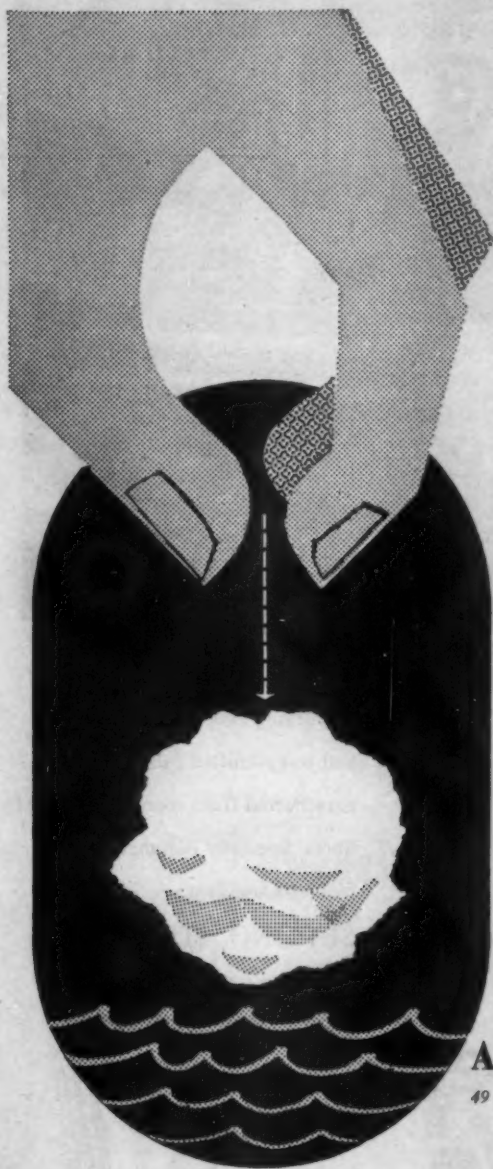
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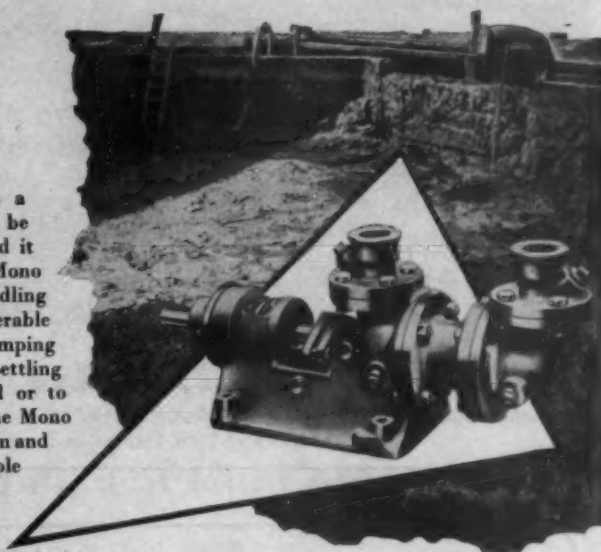
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## Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

### LECTURES

Control of Reducing Agents in Vat Dyebaths  
Dyeing of Orlon and Orlon Mixtures

*W. J. Marshall*  
*I. M. S. Walls*

### F.T.C.C. PUBLICATION

Influence of Temperature and Humidity on Fading

*P. W. Cunliffe*

### COMMUNICATIONS

Package Dyeing—II

*W. Armfield, J. Boulton, and J. Crank*

Interaction between Chlorazol Sky Blue FF

and Chrysophenine G in Aqueous Solution *A. N. Derbyshire and R. H. Peters*

Identification of Vat Dyes

*D. A. Derrett-Smith and J. Gray*

Detection of Dyes possessing a *p*-Phenylenediamine


or a *p*-Nitroaniline Structure

*F. Feigl and C. C. Neto*

Polarographic Contribution to an Investigation of

Fur Dyes and their Oxidation Products

*G. Sandberg*



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# THE JOURNAL OF THE Society of Dyers and Colourists

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Volume 72 Number 4

APRIL 1956

Issued Monthly

## Proceedings of the Society THE TWELFTH JOHN MERCER LECTURE

### Modern Resin Finishing of Textiles Practice and Research

G. LANDELLS

*Meeting held at the Midland Hotel, Bradford, on 17th March 1955,  
Mr. Fred Smith (President of the Society) in the chair*

The lecture surveys the development of the application of synthetic resins to textiles and the inter-relation of practice and research. Resin application developed first on two main lines, viz. the use of emulsions of preformed vinyl-type polymers and the urea-formaldehyde crease-resist process. By using different preformed vinyl polymers a wide variety of finishes may be obtained, whereas the urea-formaldehyde finish, which is a key finish both practically and theoretically, is itself the basis of many finishes and has been the pattern for many other types of amino-formaldehyde resin finish. The importance of the location of the resin in or on the fibre is demonstrated in numerous systems. The use of resins for modifying handle, for imparting crease-resistance or dimensional stability, or for fixing embossed effects is now standard practice, but synthetic resins are finding increasing use in new outlets. Thus, phosphorus compounds are now being incorporated with the amino-formaldehyde type of resins to produce anti-flame finishes. Research is proceeding in the field of isocyanate chemistry, especially on polymer formation in and on textile fibres, and some progress is being made in practical application. A new class of polymeric substances—the silicones—has opened up a completely new field in the progress of water-repellency. It is shown that resin application to textiles is now a specialised study and that many more new developments may be expected.

It has often been stated that Industry requires more trained scientists to assist in bridging the gap between academic research and industrial practice. This presupposes that results of academic research can be readily turned into industrial practice. It is popularly held that progress occurs in this way and that, if only the practical men could fathom the tortuous workings of the pure scientists, then progress would be remarkably rapid. In fact, in my experience of textile technology, practice has frequently developed out of accidental discovery or *ad hoc* work rather than planned research. This is certainly true of the branch of technology we are to consider this evening. However, research has followed up, extended, and explained the workings of many of our processes, giving us a better understanding of them and clearer leads for future development. I have decided, therefore, to attempt the task of linking practice and research by looking into both camps. I believe that this is best done by giving an account largely of my own experiences and observations, some of them unpublished, and those of my collaborators and colleagues, both in research and in the works. In particular, I would

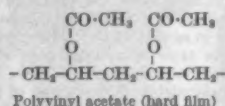
like to draw on those processes and results which illustrate important principles in textile finishing. In this way I hope to avoid a stereotyped discussion of resin application. In pursuing these aims, therefore, I would like to discuss firstly some practical points.

In the early days of the application of synthetic resins to textiles, two main classes of products emerged—on the one hand, emulsions of vinyl-type resins, the production of which was largely conditioned by the requirements of the plastics industry; and on the other hand, precondensates of the urea-formaldehyde type, inspired by the success of the Tootal Broadhurst Lee crease-resist process. Application and study of these laid the basis for the development of resin finishing. The first important generalisation was that preformed resins of the vinyl type were located on the fibre surface and, because of their film-forming and adhesive properties, produced firm or full finishes by gumming together the fabric structure. The precondensates, on the other hand, were found to penetrate the individual fibres and give flexible finishes with crease-resist and/or swelling-resistant

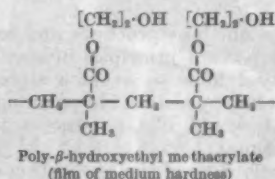
properties. These early developments were undertaken largely on cellulosic fabrics, with subsequent attempts to develop finishes for wool. Since then, further attempts have been made to improve on the performance of these established materials, and some interesting suggestions have been made in recent years. The appearance of the ethyleneimine derivatives<sup>1</sup> just after the 1939-1945 world war broke new ground, but finishes based on these do not appear to have come to maturity. However, a number of new materials do look as though they have come to stay. The silicones, for example, are becoming well established for water-repellency, and older resins in new guises, e.g. the acid colloids of melamine-formaldehyde resins, are proving useful in works practice. In the new phase of resin chemistry now developing, wider classes of textiles are being processed. Not only is viscose rayon widely treated, but also cotton to an increasing extent, and among the synthetic fibres particularly nylon, as well as the various mixture cloths such as wool-viscose rayon and Terylene-viscose rayon, which are being encountered in increasing quantities by the finisher.

#### VINYL-TYPE RESINS

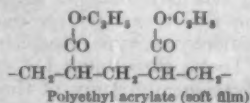
Preformed vinyl polymers have been used successfully in textile finishing to give increased weight and firmness to fabrics. An idea of their behaviour on fabrics may be obtained by drying down the dispersions and examining the physical properties of the films. A hard brittle film such as that given by polyvinyl acetate—



will give a stiff finish, whereas the flexible film from  $\beta$ -hydroxyethyl methacrylate—



will give a firm, flexible finish of medium stiffness. A soft film, such as that given by polyethyl acrylate—



will give a limp, full finish.

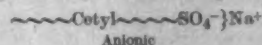
Preformed polymers of this type are not completely fast to washing, but are less readily removed than the older fillers such as starch.

It may generally be said that the finished fabrics show properties which are a blend of those of the resin film and of the fabric itself. We cannot at too early a stage stress the importance of the location

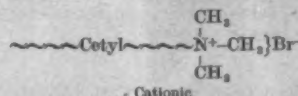
of the resin even in the case of preformed polymers. The location of the resin with respect to the fabric is of importance. If, for example, an emulsion of polyvinyl acetate is thickened with a little cellulose ether and the resin film is persuaded to sit on the surface of certain fabrics by first giving the fabric a non-absorbent finish and then applying the resin by back-filling, a crisp and papery finish is obtained. This has been called "crackle" finish. If the same fabric is padded through the thickened dispersion, a totally different result is obtained: the resin has penetrated the fabric structure and the "crackle" has disappeared. Similarly, if a fabric which has been back-filled in the way described is hot-calendered, the handle is completely modified. The resin appears to sink into the fabric structure, again with loss of "crackle". These are examples of the importance of method of application.

Vinyl polymers, however, do not usually find as great an outlet in mechanical finishing as do the condensation resins, though at least one useful finish may be mentioned. On certain cotton lining fabrics a resin such as polyvinyl acetate together with a Schreiner finish gives a useful effect. There is some evidence of increased abrasion resistance and there is considerable enhancement of appearance.

Vinyl resin particles in dispersion may be positively charged or negatively charged depending on the type of dispersing agent used. If the agent is of the type of cetyl sodium sulphate—



the resin particles will be held in suspension by the long-chain negative ion, and the dispersion will be of the anionic type. If the agent is of the type of cetyltrimethylammonium bromide—



a positively charged or cationic dispersion is obtained.

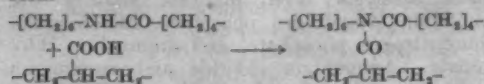
Application of a positively charged dispersion to nylon hose has given a useful anti-sag finish. In this form the resin particles exhaust on to the nylon fibres. Resin may actually precipitate from an anionic dispersion to give a dulling effect if fabric is first impregnated with a cationic auxiliary product<sup>2</sup>.

Having both positive and negatively charged dispersions at his command enables the finisher to solve many difficult compatibility problems where combined finishes are required.

Another vinyl resin finish which does not depend simply on a blend of resin and fibre properties, but appears to be an example of resin-fibre interaction, is that given by polyacrylic acid on nylon. This substance, which is water-soluble because of its carboxyl groups, is applied by padding and drying. It may then be increasingly insolubilised with increasing baking temperatures. One possible mechanism<sup>3</sup> is interaction between the amido

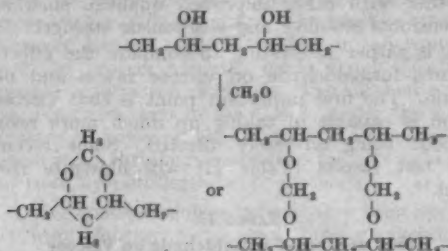


groups of nylon and the carboxyl groups of the resin—



In practice this can produce another crisp finish and is one method of obtaining the so-called "crinoline finish" on nylon.

Yet another finishing principle forms the basis of the application of polyvinyl alcohols to give crisp finishes. Here the polymer is water-soluble and may be applied to the fabric at the pad mangle. If formaldehyde is incorporated, then insolubilisation of the polyvinyl alcohol<sup>4,5</sup> occurs on subsequent stenter drying, and a wash-resistant finish is obtained—

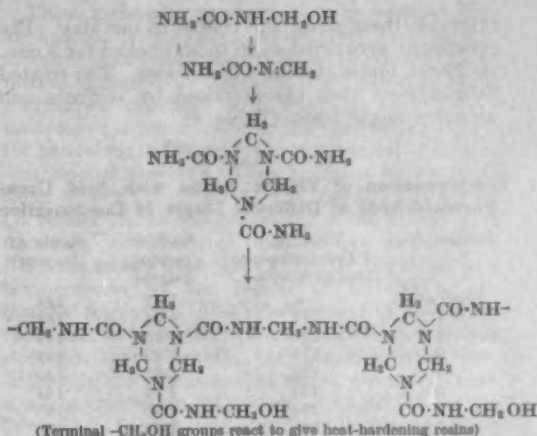


Other cross-linking agents which will cause fixation of this polymer are bishydroxymethylurea and glyoxal. Polyvinyl alcohol is particularly useful for giving a crisp finish to fabrics; thus crêpe fabrics composed of acetate rayon, viscose rayon, or mixtures of both may be rendered more like taffetas, i.e. given a "taffetised" finish.

Application of vinyl resins from organic solvents has found little use. However, the overall picture is one of remarkable variation. Resins may be stiff, rubbery, or soft, they may be plasticised to various degrees, they may be water-insoluble and in emulsion form either negatively or positively charged, they may be water-soluble and capable of insolubilisation, they may be used for modifying handle, i.e. as "synthetic starches" or as binding pigments or bonding agents.

#### CONDENSATION-TYPE RESINS

Most textile chemists know the simple outline of urea-formaldehyde condensation which appears in all good lectures on resin application, namely the initial alkaline reaction between urea and formaldehyde to give hydroxymethyl compounds. This step is essential for controlled condensation, otherwise premature precipitation of compounds of low molecular weight occurs. After hydroxymethyl formation, an acid or so called potentially acid catalyst is added, and immediately a condensation reaction sets in. Various attempts have been made to determine the chemical nature of the resin produced, and a number of formulae may be drawn<sup>6,7</sup>. Perhaps the one based on the soundest chemical evidence is that of Marvel<sup>8</sup>, who believes that a structure of the following type is formed—



However, the resin is obviously complex, and no one can say with certainty what its structure is.

An understanding of the course of the urea-formaldehyde reaction for textile application is best obtained by getting a picture of the viscosity changes which occur. I employed this method in the laboratories of Imperial Chemical Industries Ltd. at Blackley in 1947. With urea to formaldehyde in the ratio commonly employed for crease-resist finishing, namely 1:1.6, in the presence of ammonia (sp.gr. 0.88), the initial condensation proceeds at room temperature to a comparatively steady state on standing overnight. It was found in various experiments that addition of an acid catalyst, ammonium dihydrogen phosphate, caused an immediate increase in viscosity, which continued steadily until clouding point was reached. The greater the quantity of acid catalyst added, the more rapidly the condensation occurred. A typical result is shown in Fig. 1, in which the viscosity (time of flow) is plotted against time.

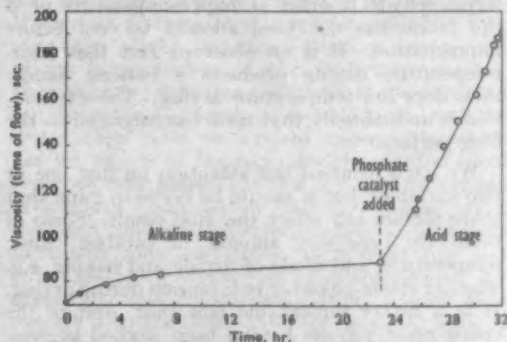


FIG. 1.—Viscosity Changes in a Urea-Formaldehyde (1:1.6) System at 20°C. (catalyst 10%  $\text{NH}_4\text{H}_2\text{PO}_4$  on weight of urea)

Fabric which is impregnated during the acid condensation is thus treated in an actively condensing system. We thought that it would be interesting to see what happened to fabrics padded in precondensates of various degrees of condensation. Specimens of a plain-weave viscose rayon staple fabric were therefore treated at

intervals throughout the course of one day. The specimens were dried at 60°C. and baked for 3 min. at 130°C. under standard conditions. The treated fabrics were then characterised by stiffness and recovery-angle tests (Table I).

TABLE I

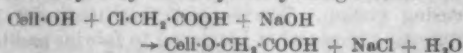
**Impregnation of Viscose Rayon with Acid Urea-Formaldehyde at Different Stages of Condensation**

Pattern No.	Viscosity of Precondensate (time of flow, sec.)	Stiffness (bending length)	Angle of Recovery
Untreated	—	1.32	108°
1	111	1.76	151°
2	110	1.83	148°
3	119	1.89	143°
4	125	2.02	145°
5	131	2.64	141°
6	134	2.96	138°
7	138	2.64	136°

It will be seen that increasing fabric stiffness is obtained with increasing viscosity of precondensate, and at the same time the fabric shows decreasing "resilience" as judged by recovery angles. That these differences were not due merely to differences in resin content was ascertained in a repeat series in which over the seven patterns the resin contents varied only between 18.3 and 19.4%.

The above results do show that differences of this sort can occur in works practice, particularly if careful control is not exercised. In practice, of course, the condensation is not allowed to proceed with concentrated reactants as in the experiments referred to. Furthermore, the catalyst is not added to the concentrated resin but to the padding mixture, which is in a much more diluted form. Differences in practice, therefore, are not as acute. The above results can mean, however, that if for any reason resin is brought to the fibre surface, then increased stiffness of handle and impairment of crease-recovery take place. This effect is obtained, for example, if fabric impregnated in urea-formaldehyde is dried at high temperature or if the fabric has not been allowed to cool before impregnation. It is an observed fact that high-temperature drying produces a harsher handle than does low-temperature drying. The explanation is undoubtedly that resin has migrated to the fibre surface.

We have focussed our attention on just one or two variables, but it should be borne in mind that other factors can affect the final result. Some of these are type and amount of catalyst; time, temperature, and mode of drying and baking, e.g. whether steam-baked or not; tension during drying. It is a rather remarkable fact that, despite the crease-resist process having been worked successfully for some twenty years, catalyst studies of the urea-formaldehyde condensation are still being pursued. The interesting suggestion of building in the catalyst by carboxymethylating cellulose—



has recently been made<sup>9</sup>, the carboxyl groups introduced into the cellulose acting as catalyst for the resin condensation. The method must be

regarded as rather academic. Among the established catalysts used in this country are ammonium dihydrogen phosphate, diammonium monohydrogen phosphate, and ammonium thiocyanate. Ammonium chloride and ammonium sulphate have been largely used on the Continent, and more recently, particularly in the U.S.A., salts of organic amines have been used to a greater extent in bulk practice. The advantages of the amine salt catalysts include improved stability of the impregnating liquor and less likelihood of tendering the fabric. However, in spite of some considerable differences in effect produced by variations in technique, the urea-formaldehyde process on viscose rayon is remarkably flexible in that within a wide range of working conditions a marked crease-resist effect may be obtained together with other improved qualities such as dimensional stability and wet tensile strength.

It is rather interesting to compare the effects of urea-formaldehyde on viscose rayon and on cotton. The first important point is that viscose rayon is capable of taking up much more resin without being adversely affected. Some recent tear test results (Table II) will illustrate this point<sup>10</sup>.

TABLE II

**Effect of Urea-Formaldehyde on Viscose Rayon and Cotton**

Treatment	Tear Strength (oz.)	
	Viscose Rayon*	Unmercerised Cotton†
Untreated	42	36
5% urea-formaldehyde	44	28
5% urea-formaldehyde, then removed by hydrolysis	38	29
20% urea-formaldehyde	40	17
20% urea-formaldehyde, then removed by hydrolysis	36	31

\* Utility Quality 1009 (staple-fibre fabric)

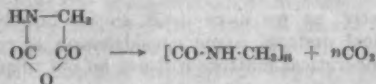
† Plain-weave fabric

Stripping urea-formaldehyde from viscose rayon causes a small reduction in tear strength, whereas with cotton tear strength, which may be markedly reduced by increasing amounts of resin, may be strikingly restored by stripping the resin. In other words, viscose rayon can "swallow" 20% on its weight of this type of resin without difficulty, whereas cotton cannot. In crease-resisting both cotton and linen it is preferable that the base materials be first mercerised, and here we have a link with Mercer. This meets one of the cardinal requirements of the crease-resist process, namely that the cloth should be thoroughly absorbent. A further feature of the crease-resisting of linen is the post-mercerising process, viz. the passage of urea-formaldehyde-treated linen down a conventional mercerising range, which is practised with a view to overcoming embrittlement. This process is designed to relax the rather rigid structure and at the same time to remove a certain amount of surface resin. For cotton and linen, therefore, lower quantities of crease-resist resin are required, and special attention must be paid to relaxation of strains. The use of softening agents is also of assistance with these fibres. On mixture fabrics,

e.g. of acetate rayon and viscose rayon, an important principle is, so to speak, to legislate for the viscose rayon content, i.e. to apply only the quantity of resin appropriate to the viscose rayon content. In a 50:50 mixture, for example, the amount of resin applied should be half that applied to a 100% viscose rayon fabric, as on drying capillary attraction causes the resin to migrate to the viscose at the expense of the acetate rayon. In mixture cloths of wool and viscose rayon, again, it is only the latter which is crease-resisted. The cloth as a whole is improved, and the lowered water-imbibition brings its properties nearer to those of wool. Addition of small amounts of water-repellent agents, furthermore, brings the repellency approximately to that of wool.

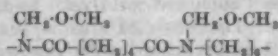
On all-wool fabrics it is the melamine-formaldehyde resins that have made most progress in preventing milling shrinkage. The handle obtained, however, has not satisfied finishers in this country, and the process has not made much headway against chlorination methods. The method which has been practised in the U.S.A. under the name Lanaset<sup>11</sup>, however, has shown how a considerable measure of shrinkage resistance may be achieved on wool by non-degradative methods.

Other condensation polymers have been applied to wool fabrics to control milling shrinkage. For example, anhydrocarboxyglycine<sup>12</sup>, which may be polymerised on the fabric by heating—



has given a superb shrink-resist finish, but because of the inherent instability of the reagent it is not a commercial proposition.

More recently another form of polyamide has been applied to wool for shrink-resistance. This is a soluble form of nylon, viz. *N*-methoxymethyl-nylon—



It really becomes effective only after it has been hydrolysed back on the fabric to the insoluble nylon form<sup>13</sup>. This is yet another example of the importance of technique in applying resins and an interesting example of getting a polymer in a suitable condition in the right place to perform its function.

Melamine can be made to condense with formaldehyde in much the same way as urea can, and no doubt viscosity changes would reveal a similar picture to that given by urea-formaldehyde. The condensation of melamine with formaldehyde, however, is not so readily controlled, and it is usual for the finisher to purchase hydroxy-methylated melamines or their methyl ethers. The manufacturers, however, are able to present a wide variety of products depending on the degree of condensation, hydroxymethylation, and methoxymethylation. The last-named is practised to assist stabilisation of the product.

These melamine products may be applied with an acid or potentially acid catalyst such as ammonium thiocyanate, ammonium dihydrogen phosphate, ammonium chloride, or more recently magnesium chloride, and, although they give a measure of crease-resistance, they are more suitable for producing wash-resistant mechanical effects or dimensional stability. They function by virtue of their ability to penetrate and harden the fibres, i.e. reduce the swelling capacity of the fibres. It is necessary in calendered finishes that no curing of the resin should take place at the drying stage, and temperatures in the region of 150–200°r. are usually employed. The effectiveness of the treatment can be balanced against the effects on tensile strength, tear strength, and abrasion resistance. Although the condensation resins generally cause a slight reduction in tensile strength of cotton fabrics, it is not unknown for increases to be observed on mercerised fabric, as shown by results taken from a bulk-scale investigation (Table III).

TABLE III

Finish	Tensile Strength (lb.) (Goodbrand constant rate of reverse)	
	Warp	Weft
MERCERISED COTTON POPLIN (122 ends and 72 picks per inch; 2/80s warp and 2/80s weft)		
No resin	285	147
5% urea-formaldehyde	344	154
5% melamine-formaldehyde	355	140
UNMERCERISED PLAIN COTTON FABRIC (72 ends and 68 picks per inch; 22s warp and 20s weft)		
No resin	200	209
5% urea-formaldehyde	193	160
5% melamine-formaldehyde	185	162

A variation on the permanent-glaze theme may be seen in the production of sculptured effects. Thus a resin of the melamine-formaldehyde type may be incorporated in a printing paste together with, say, a pigment. Stripes may be printed and the fabric baked to cure the resin as usual. If the cloth is then placed in caustic soda of 53°Tw., shrinkage of the imprinted portions occurs and results in puckering of the unshrunk portions. If a design is printed on the fabric, the background can be made to shrink in caustic soda, and the design then takes on a raised appearance, which has led to use of the term *sculptured effect*. Not everyone may know that this is a modern version of a finish practised by Mercer. Instead of a hardened condensation resin, he used as his resists to caustic soda such gums as Senegal gum and gum arabic<sup>14</sup>, which acted mechanically by preventing the caustic soda from coming into contact with the fibres. The fundamental basis of the process, however, remains much the same.

Yet another variation on the embossing theme is to employ in addition to the normal embossed design a means for tipping the raised portions with special inks, containing resins and pigments. A device may also be employed which inks the embossing roller, which thereby applies colour to the hollows. Fabrics so treated are finally baked to fix the design and the resin-bound colours.

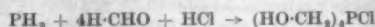


In this way really beautifully decorated fabrics may be obtained.

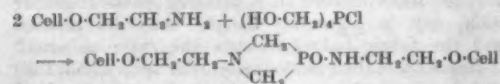
#### FLAMEPROOFING WITH RESINS—T.H.P.C.

A number of resin methods have been tried hitherto for producing flame-resistant finishes. The value of polyvinyl chloride and other halogenated substances such as chlorinated paraffin wax, particularly in conjunction with inorganic pigments, e.g. antimony oxide, has been recognised. Generally, these finishes, to be effective, overload the fabric and render it unsuitable for most normal textile uses. Another resin method, developed by Bowen, Majerus, and Meals<sup>15</sup>, was based on a condensation product of dicyandiamide and formaldehyde. About 30% of the resin was applied by padding, and the fabric then passed through 0.5 N. sodium hydroxide solution, dried, and heated at 150°C. for 5 min. A substantially water-resistant flameproof material was thus obtained. It fell short only in complete resistance to hot soaping.

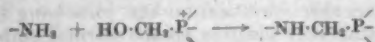
A modern method of flameproofing, involving synthetic resins which possess a high degree of wash resistance, is the use of tetrakis(hydroxymethyl)phosphonium chloride (T.H.P.C.) in conjunction with amino-formaldehyde resins. T.H.P.C. is prepared in aqueous solution from phosphine as follows—



and its application to cellulosic textiles for flameproofing was first suggested by Reeves and Guthrie<sup>16</sup> in the U.S.A. These workers are known for their work on the amination of cotton, and it is probable that interest in T.H.P.C. arose from reaction between it and aminised cotton. The following possible reaction has been suggested by Reeves and Guthrie—



The resulting phosphorus compound was found to be stable to boiling sodium hydroxide solutions. It was also found possible to flameproof cotton without having to carry out the initial amination, and polyfunctional amines such as melamine were used. T.H.P.C. can react with either melamine or urea to give polymers capable of flameproofing cellulosic fabrics. The preferred method at present involves the co-condensation of T.H.P.C. with hydroxymethylmelamine within the fibres. One would expect reaction between the amino groups of the resin and the hydroxymethyl groups of T.H.P.C. to be on the following lines—



the reactions occurring during the condensation involve also the splitting off of hydrochloric acid and one molecule of formaldehyde, and subsequent oxidation of the trivalent phosphorus to its quinquevalent state.

In practice, the T.H.P.C. is first neutralised with triethanolamine, the function of which is to retard condensation. Urea is then added to buffer the hydrochloric acid produced during the condensation. Finally a hydroxymethylmelamine precondensate is added. Fairly considerable quantities of the resin, 10–30% depending on the fabric, have to be applied, but the resulting flameproof result is excellent. We have seen it withstand as many as fifteen launderings at the boil without loss of flameproof effect. Even though a certain flaming and charring occurs, there is a complete absence of afterglow. Naturally, the loading of cotton with such high quantities of resin causes a reduction in rip strength, and therefore care and control are required during processing. Nevertheless, because its advantages greatly outweigh its disadvantages, bulk-scale processing has commenced with this finish.

\* \* \*

We have considered so far external application of vinyl polymers and internal application of amino-formaldehyde condensates. A trend over the last few years has been to turn attention to precisely the reverse aspect of resin application. In short, an increasing number of practical processes depend on external application of the condensation resins, and research workers have turned their attention to lodging vinyl polymers inside fibres. Progress in these two fields will therefore be discussed briefly.

Firstly, as we have dealt so far largely with practical matters, some consideration of research and theoretical matters will not be out of place.

#### INTERNAL DEPOSITION OF VINYL POLYMERS

Realisation that the formation of hard and water-resistant resins of the urea-formaldehyde type inside fibres gives valuable technical effects led research workers to attempt to form resins of the vinyl type inside fibres. Little success was achieved until Speakman and Lipson<sup>17</sup> at Leeds University devised the "anchored catalyst" technique with wool fibres. The basis of this is that the wool fibre is first impregnated with one member of a catalyst combination, namely a ferrous salt, and then with a vinyl monomer together with the second component of the catalyst, the idea being to limit polymerisation to the inside of the fibre. Speakman and Lipson produced evidence that resins were built up in this way, and wool fabric so treated showed resistance to shrinkage. In another series of experiments<sup>17</sup>, methacrylamide was built up in wool fibres into polymethacrylamide, which because of its chemical nature conferred resistance to acid dyes. Thus was born a general method of forming vinyl resins inside fibres.

Following the publication of the method, I succeeded in forming a polymer from  $\beta$ -hydroxyethyl methacrylate inside viscose rayon, using as the catalyst system sodium hydrosulphite and ammonium persulphate. With viscose rayon the fibre dissolution technique using cuprammonium hydroxide was available, and evidence was soon obtained that internal protection had resulted.



Subsequently, swelling, staining, and X-ray experiments, carried out with Professor C. S. Whewell at Leeds University, proved beyond doubt that vinyl resins were lodged inside the viscose rayon fibre<sup>18</sup>. As further evidence, if any were needed, the vinyl resins blow up or distend the viscose rayon fibres.

It was disappointing to find, therefore, that, as far as could be judged, there was little promise with the vinyl resins chosen of achieving much swelling resistance or dimensional stability in viscose rayon. No crease-resistant effects were observed. Even had technical promise existed, the method of application would have to be batchwise, and at present this means of forming polymers inside fibres still remains rather academic. However, there has appeared recently a vinyl resin polymerisation method<sup>19</sup> which is claimed to give a wash-resistant anti-static finish to synthetic fibres. The nature of the monomer has not been revealed, but the important observation is that, after catalysis with potassium persulphate, the activated solution may be used up to 48 hr. later. With times of this order progress with vinyl monomers might well be made other than in the laboratory.

#### THEORETICAL ASPECTS OF CREASE-RESISTANCE

Why is it, if we have lodged vinyl resins in cellulose, that crease-resistance is not achieved? Is it because the urea-formaldehyde resin cross-links the fibre and the vinyl resins do not? This is one possible explanation, but before one jumps to such a conclusion the various ways in which crease-resistance may be produced should be considered. Just how careful one has to be in ascribing crease-resistance to covalent cross-linking is shown in the first place by the wide variety of agents which can be used to impart resistance to creasing. Certain inorganic salts, glyoxal, and even oxidation with periodic acid are effective. I was able to show this last effect in 1946. Results of crease recovery tests on viscose rayon (Utility Quality 1005) oxidised for 24 hr. in periodic acid buffered to pH 4 showed marked increase in recovery (e.g. Table IV).

TABLE IV  
Crease Recovery of Viscose Rayon

	Recovery Angle	
	Warp	Weft
Untreated viscose rayon	117°	109°
Periodate-oxidised viscose rayon	156°	155°

The action of inorganic salts and glyoxal may be explained by electrovalent cross-linking, but it is difficult to see how this could operate with the oxidation treatment.

In the second place, urea-formaldehyde can actually produce some crease-resistance in glass fabric, where penetration, let alone cross-linking, is impossible. There is an overall springiness, and measurements of recovery angle (made on the Shirley instrument) confirm this (Table V).

TABLE V  
Crease Recovery of Glass Fabric\*

Finish	Recovery Angle	
	Warp	Weft
Untreated	136°	128°
1% urea-formaldehyde resin	170°	168°
2% urea-formaldehyde resin	161°	150°
3% urea-formaldehyde resin	161°	160°

\* 56 ends and 52 picks per inch; 3/22s warp and 3/21s weft; 8-49 oz./sq. yd.; weave 8-shaft venetian

On balance, therefore, it appears that the crease-resist effect produced by urea-formaldehyde can be adequately explained by the physical properties of the resin lodged inside the fibres without invoking reaction with the cellulose.

#### EXTERNAL APPLICATION OF THERMOSETTING RESINS

A feature of the urea-formaldehyde condensation is that products of various degrees of condensation may be obtained and that stabilised forms of higher molecular weight are available in the form of syrups from a number of manufacturers. These urea-formaldehyde syrups may be used alone and give stiff but non-crease-resistant finishes to cellulosic fabrics. Small quantities may be added to crease-resist mixtures to give added weight or stiffness as required. Curiously, when we come to nylon it is not these urea-formaldehyde syrups of higher molecular weight that are most effective in producing wash-fast stiff finishes, but rather the precondensates of lower molecular weight and in particular those of melamine-formaldehyde.

If weak acids such as acetic and formic are added in certain proportions to hydroxymethylmelamine derivatives and the system is allowed to age, then condensation may proceed a stage further, as is shown by the development of a colloidal haze<sup>20</sup>. The resin is now in the "acid colloid" form and may possess considerable stability depending on the type of acid employed. We found that with certain proportions of acetic acid there was a tendency to gel on standing in the open, but if we kept the colloid in a sealed bottle or carboy it remained perfectly stable for months.

Various acids may be employed to produce resin colloids, a notable one being gluconic acid or its  $\delta$ -lactone. This has the advantage for treating textiles that a very mild acid is employed. The method is not, however, restricted to weak acids, as hydrochloric acid is effective. It is an odd feature that too much acid may cause instability, and so may too little. Products obtainable range from typical blue hazy dispersions to gels on the one hand and milky dispersions on the other. The more complete physicochemical picture of such a system shown in Fig. 2 has been taken from the patent literature<sup>21</sup>.

We shall refer to the melamine-formaldehyde resins which give the blue colloidal haze simply as acid colloids. It has been found that in this state the particles are positively charged. Indeed, the melamine-formaldehyde resins in the acid-colloid form provide quite a few surprises. On application

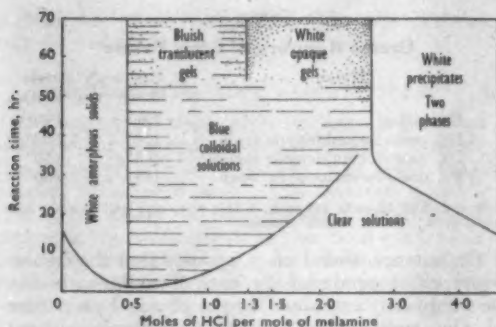


FIG. 2.—Effect of Hydrochloric Acid on Melamine-Formaldehyde Resin (15% solids) at 25°C.<sup>21</sup> (Reproduced from BP 623,355 by permission of the Controller, H.M. Stationery Office)

to cotton or viscose rayon they have a marked stiffening effect, so much so that above 5% applied resin the fabric readily cracks and possesses a boardy handle. Our attempts to apply them to nylon for stiffening have failed. This lack of affinity may be a question of the respective charges of the fibre and the resin particles, or one of lack of adhesion to the extremely smooth nylon fibres. On cellulosic fabrics the resin is remarkably fast to washing for a surface-application resin. Indeed, it has been described as being midway between the thermoplastic class and the thermosetting class in its action, and our experience confirms this as a neat summary.

Another surprising finding was that, not only could a positively charged acid colloid be blended with a positively charged dispersion of a vinyl resin, but it could also be blended with a negatively charged dispersion of polyvinyl acetate. A finish based on the latter mixture proved particularly useful in dealing with acetate-viscose rayon mixture fabrics. The thermoplastic resin appeared to take care of the acetate content, and the acid colloid the viscose component. It would seem that there are several problems here which would be worthy of the attention of the academic research worker.

#### ORGANIC ISOCYANATES

We have seen a tendency for a breaking down of the strict differentiation between surface and internal resins, and further evidence of this comes from the isocyanate field. The organic isocyanates form a large group of chemicals as yet only little exploited by the textile finisher. The most common are those prepared from hexamethylenediamine and *m*-tolylenediamine, viz. hexamethylene diisocyanate (H.M.D.I.) and *m*-tolylene diisocyanate (M.T.D.I.). As prepared they are pungent, rather obnoxious liquids which are chemically very reactive. Their application to textiles may be simply effected by dissolving them in an organic solvent such as benzene, toluene, or petroleum spirit and passing fabric through the solution; the fabric is then dried and finally baked. Alternatively, they may be emulsified, and fabric padded in the emulsion before drying and baking. A third method of application is first to treat the

isocyanate with sodium bisulphite, when a water-soluble salt is formed.

The three methods of application have different effects on viscose rayon fibres, as can be seen from the cuprammonium test. This test shows that solvent application gives merely a thin surface sheath (see Fig. 3 and 4), which probably consists of closely adhering polymer but could possibly be cellulose insolubilised by a very limited penetration of the isocyanate. Certainly, virtually all of the fibre dissolves. With fibres treated by emulsion application the fibre disrupts in the swelling agent and shows an insoluble central region bursting through a skin or surface sheath. With urea present in addition, the central core is more solid (see Fig. 5). With the isocyanate applied in the form of an aqueous solution of the bisulphite addition compound complete penetration occurs, as shown by the appearance of a homogeneous, highly swollen gel in the test. A stronger, more swelling-resistant jelly is obtained if the bisulphite addition compound is applied in the presence of urea (see Fig. 6). This gradation in the degree of penetration was observed with hexamethylene diisocyanate and its bisulphite addition compound, and is reflected in certain technical results, e.g. the relative stability to washing of fabric treated with H.M.D.I.-bisulphite in the absence and presence of urea.

It is surprising that solvent application of isocyanates to cotton after a mechanical finish confers a high degree of wash resistance on that finish<sup>22</sup>. Thus we have an example of what appears to be a surface resin conferring wash resistance on mechanically produced effects.

If a cellulosic fabric which has been impregnated with an isocyanate-bisulphite adduct of the type described, or even better with isocyanate-bisulphite and urea, is given a mechanical treatment such as a glaze before baking, then that glaze may be retained in good measure on washing<sup>23</sup>. It has been suggested by Bayer<sup>24</sup> that the bisulphite adducts are isocyanate splitters. Although this may be so, there is no marked isocyanate odour on heating the adducts of H.M.D.I. or M.T.D.I., and it may be that the adducts on heating are immediately transformed into polymeric forms. As evidence of this, fabrics which have been treated with the bisulphite adduct and then heated are found to possess affinity for acid and certain direct dyes, very heavy dyeings being obtainable. Increasing the time or the temperature of baking produces an increasing capacity in the fibres for absorbing acid dyes. When urea also is present, a point is reached when the dye affinity falls off again. This could be due to further hardening of internally deposited polymer with disappearance of groups responsible for the affinity for the dyes, by analogy with the behaviour of urea-formaldehyde under somewhat similar conditions. The effect described contrasts with the surface application of isocyanates, which gives quite a marked resist effect to dyes.

The isocyanates may be used to improve the fastness of dyes and pigments. In particular, we

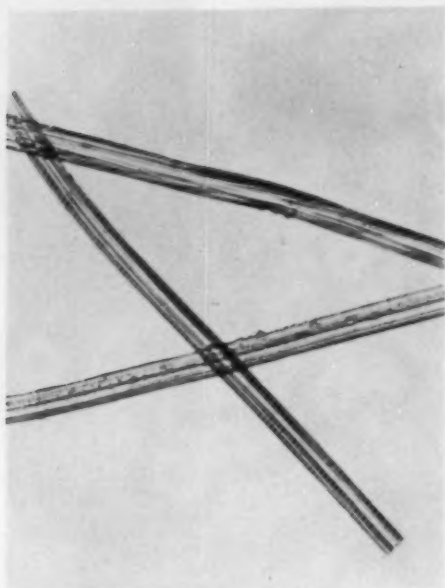


FIG. 3—Untreated Viscose Rayon Fibres in Water  
(Control for Fig. 4-6)

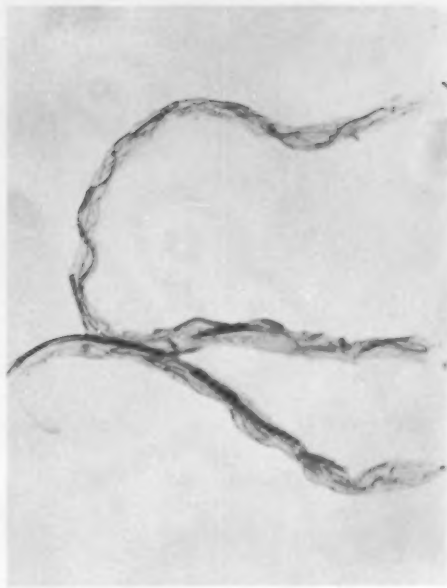


FIG. 4—Viscose Rayon Fibres treated with Hexamethylene Diisocyanate from Solvent—partly dissolved in Cuprammonium Hydroxide to leave a "Surface Sheath"

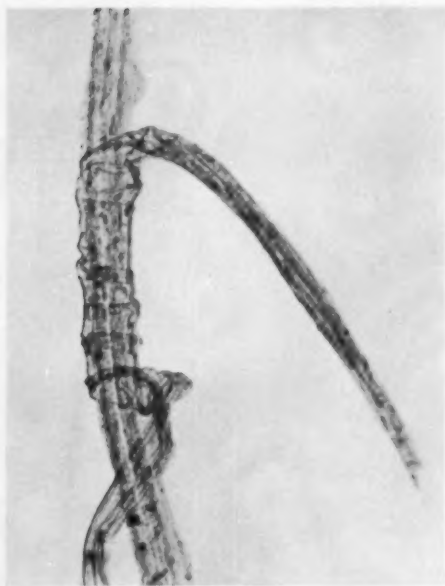


FIG. 5—Viscose Rayon Fibres treated with Urea and Hexamethylene Diisocyanate from Aqueous Emulsion show both an Insoluble Core and a Surface Sheath in Cuprammonium Hydroxide

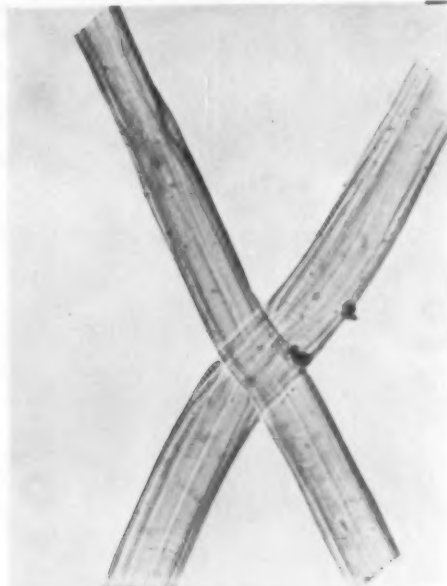
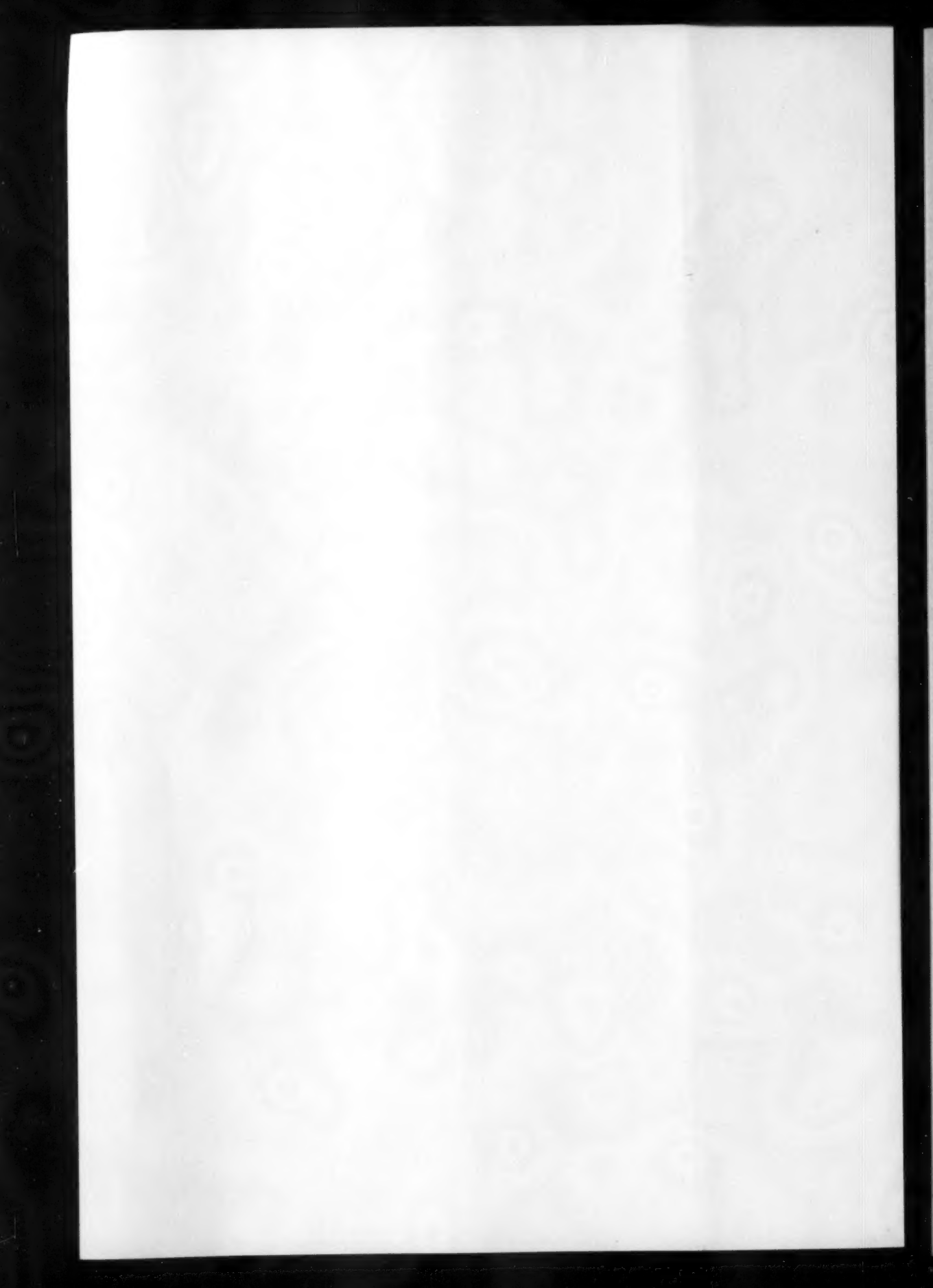


FIG. 6—Viscose Rayon Fibres treated with Hexamethylene Diisocyanate-Bisulphite Compound and Urea give a highly Swollen Gel in Cuprammonium Hydroxide

Magnification  $\times 230$





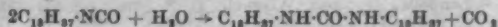
have found chlorophenylene diisocyanate to possess a considerable measure of pigment-binding capacity without addition of other binders.

isocyanates are being utilized in another type of application. Thus the normal drying oils used to produce transparent effects on silk have poor adhesion to nylon and Terylene, and polyisocyanates are being used to harden polyester resins to give transparent films of excellent adhesion. These so called "oiled silk" effects may be obtained by conventional techniques.

Other workers<sup>25</sup> have recently attempted to utilize isocyanates also for producing water-repellency. Thus in the U.S.A. a reassessment of the method of linking long-chain compounds by means of the isocyanate group has been tried with the commercial appearance of octadecyl isocyanate. The idea was that cellulose would react as follows—



It was concluded, however, that a large part of the water-repellency was due to the formation of insoluble dioctadecylurea by hydrolysis of the isocyanate—



This finish was considered to be "shower-resistant" but not suitable for use in heavy rainstorms.

A start has thus been made in the exploitation of this promising but difficult field of resin application, and with the advent of cheaper and more plentiful raw materials further practical advances will become possible.

#### SILICONES

The problem of water-repellency brings us to another vast field of activity, namely that of silicone development. A few years ago certain organosilicon compounds became available to the textile trade and, although producing good water-repellency, made little progress because in the particular form in which they were supplied hydrochloric acid was liberated during their application. Advances here have been mainly due to the efforts of chemical manufacturers, who have now produced agents in polymeric form free from this disadvantage. A quick survey of the chemistry will make the position clear.

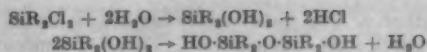
When silicon tetrachloride is placed in water a vigorous reaction occurs and hydrochloric acid is given off with much fuming—



The orthosilicic acid  $\text{Si(OH)}_4$  splits off water, and silica or sand is regenerated—



Now, if the silicon tetrachloride be substituted—and this is where the chemical manufacturer exercises his skill—various starting products for silicone preparation are obtained. Certain of these may be represented by the formula  $\text{SiR}_2\text{Cl}_2$ , where R may be methyl, ethyl, phenyl, or other radical. If these products are now allowed to drip into water, instead of silica there is obtained a "silicone"—



Further splitting off of water produces long-chain molecules.

In this way there are produced the silicone fluids, which possess water-repellent properties but are removed by dry cleaning. It was not until a resin containing both methyl groups and hydrogen atoms attached to the silicon was produced that a satisfactory water-repellent finish was obtained. Certain commercial agents at present being successfully used are oily liquids based on polymers containing the unit  $[-\text{SiH}(\text{CH}_3)\text{-O-}]_n$ . In practice they may be applied from solutions in organic solvents by padding so that about 2% of silicone solids are deposited on the cloth, which is dried and baked to develop the full fastness properties of the silicone resin. It has been found advantageous to add a small quantity of an organometallic catalyst to assist complete polymerisation of the silicone. So far, two that are used in practice are zinc 2-ethylhexoate and tetrabutyl orthotitanate<sup>26, 27</sup>. When these catalysts are employed water-repellency is enhanced. Just as wax requires aluminium acetate to develop its full repellency possibilities, so does the silicone benefit from the use of particular organometallic compounds.

The low surface tension of the silicone solution no doubt assists the wetting of individual fibres, and the silicone forms a continuous sheath of resin round each fibre<sup>28</sup>. This has been clearly shown on acetate rayon by simply dissolving away the fibres with acetone. Because in effect each fibre is coated with a lubricant, the handle and the draping qualities of silicone-treated goods are excellent. This lubrication can, however, be a disadvantage when a tendency to slip is inherent in the particular fabric structure, and non-slip agents of the colloidal silica type may be required to correct this tendency.

The thin film of silicone adheres so firmly to the textile fibre that it is difficult to remove by means of solvents and indeed the usual chemical reagents. The rather drastic procedure of using hydrofluoric acid is necessary in order to strip the finish.

Discussion of silicone application would not be complete without reference to the emulsion method. Water-in-oil emulsions may first be made with the aid of certain heat-decomposable emulsifying agents such as cetyldimethylbenzylammonium chloride (C.D.B.A.C.), and these after passing through a colloid mill are further diluted with water to give oil-in-water emulsions. Such an emulsion has recently become commercially available and may be mixed with urea-formaldehyde crease-resist liquor and suitable catalysts. A one-bath crease-resist and silicone water-repellent finish has thus become possible<sup>29</sup>. Although the finisher has further tools here at his command, nevertheless great care and control must be exercised because of questions of stability.

#### CONCLUSION

In my early experiences of resin finishing the situation was dominated by the preformed thermoplastics and the crease-resist finish, and it seemed

rather a long time before we really broke fresh ground. At present the silicones represent a completely new class of polymeric compounds applicable to fabrics. Titanium and other organo-metallic compounds are creeping in. Phosphorus-containing polymers have already made their mark. The epoxy resins, which have not been discussed in this paper, are undoubtedly only in their infancy and may yet make their mark on the textile trade. It is quite feasible that new vinyl monomer reactions will take reactive groups into the heart of various fibres.

There is a vast and exciting field for the research worker, the application chemist, and the textile technologist, not forgetting the engineer, in developing methods and techniques for the application of synthetic resins.

I believe that many of the answers to such problems as improved wear resistance, degradation to various agencies, improved fastness of colours, water-repellency, fabric stabilisation, and flame-proofing will be provided from the resin field. Perhaps a future Mercer Lecture will tell the world exactly how!

\* \* \*

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## The Classification of Dyes by their Dyeing Characteristics

W. BEAL

*Meetings of the Huddersfield Section held at the Co-operative Society Café, Huddersfield, on 16th November 1954, Mr. J. Calvert in the chair; and of the Midlands Section held at the King's Head Hotel, Loughborough, on 23rd February 1955, Mr. S. R. Meadows in the chair*

The methods used for preparing classifications of dyes for application to wool and cotton are reviewed, and particular reference is made to the graphical representation of dyeing characteristics.

Today many different types of fibre, of greatly differing chemical structure, are available to the textile industry. Since no fibre can acquire great commercial significance unless it can be coloured by some fairly simple and straightforward process, it follows that there must be several ranges of dyes available, each tailored to serve a particular purpose—that of dyeing one or more of these groups of fibres.

From the dyeing point of view, textile fibres can be divided very broadly into three classes—

- (1) Protein fibres, e.g. wool and casein
- (2) Cellulosic fibres, e.g. cotton and viscose rayon
- (3) Acetate rayon and the newer synthetic fibres, e.g. nylon and Terylene.

These divisions are not so watertight, however, that dyes which may be applied to one group necessarily cannot be applied to another; thus many direct cotton dyes will dye protein fibres in addition to all forms of cellulose and can be used also on some of the newer polyamide fibres. A further complication is that each of these groups contains many different fibres, which are themselves quite individual in their dyeing properties.

It is therefore essential that, before we proceed to classify dyes according to their dyeing properties, we should clearly state which fibre is to be used as the basis of this classification. It does not follow that the classification evolved will be of use only for the one fibre on which the tests have been made, since the same general scheme may apply to several

other fibres which are chemically similar; but the details of this classification will normally apply only to the fibre under test.

The fibre having been chosen, the various dyes can be quickly sorted into broad groups according to the type of method which has to be used to apply them successfully, e.g.—

For wool, acid and chrome

For cotton, vat, azoic, and direct.

The next step is to examine each group separately and pick out the features on which satisfactory application primarily depends.

Most dye manufacturers put their dyes into classes and give instructions for their application in the corresponding pattern cards. One may well ask why it is necessary to go into further detail than is given by such a broad classification, but those who have had practical experience of dyeing know only too well that individual dyes vary greatly. A dyer of experience can usually handle dyes with much greater ease than can the apprentice, but even so he often gets into difficulties when using a new dye. Experience in the application of any particular dye makes it easier for the dyer to apply this dye satisfactorily, for he then knows the characteristics of the dye and can plan his dyeing method accordingly. Such experience, however, is usually acquired only by long and costly experiments, and it is obviously desirable that a system should be devised by means of which this information may be made readily available to all.

It is now necessary to decide just what form the classification is to take. Obviously, in general a comprehensive system of classification for each type of dye on the fibre chosen is desirable, but for some purposes this may be too detailed. Dyes may be classified with regard to one single feature of interest for a particular purpose. For example, classification of direct cotton dyes according to their substantivity at low temperatures would be of interest mainly to the dyer of cotton-warp piece goods, who would have no other requirement for direct cotton dyes and would therefore have little interest in any other features they might possess. Such a classification has been made, but we will later see how this has readily been achieved by utilising work carried out on a much more comprehensive classification.

The main purpose of any classification is to aid the dyer in producing level results. This is of paramount importance, since, although there will be a sale for textiles which are a little off-shade or perhaps of inferior fastness, there will be no ready market for goods which are dyed unlevel. We should, therefore, first study what are the factors which control level dyeing.

Many workers have previously studied this subject, and the conclusions generally reached are that level dyeing is mainly a function of two properties—

- (1) Rate of exhaustion
- (2) Degree of migration.

Those dyes which possess excellent migration can usually be dyed level simply because of this feature, any initial unevenness being later corrected by prolonging the dyeing process for a sufficient length of time to enable dye to migrate from the heavily dyed portions to those dyed to a lighter colour. On the other hand, those dyes which possess poor migration can often be dyed level by so controlling the rate of absorption that the dye is taken up slowly and evenly by the fibre. It therefore follows that it is necessary to classify dyes according to their rate of migration and, further, to indicate how a slow and even uptake of dye can be produced, especially with dyes which have poor migration.

With such a wide range of fibres and dyes available, it is obviously not possible, in the space available, to discuss in great detail all the possible combinations. It is therefore proposed to deal in detail with only three main classes of dyes and two fibres—

Acid and chrome dyes on wool

Direct cotton dyes on cotton.

### Wool Dyes

In 1950 a committee of the Society put forward a system of classifying acid dyes for wool<sup>1</sup> which enables them to be grouped under five dyeing methods and to be classified on a 1–5 scale according to their degree of migration under these dyeing conditions. The committee also noted that it would be advisable to provide a rate-of-strike test in order to show the speed at which dyes are absorbed by the fibre, but they did not proceed any further with this work.

A later paper, by Kramrisch<sup>2</sup>, carried this classification a stage further by measuring the effect of various shrink-resist processes on migration and exhaustion.

Other workers have classified wool dyes on similar lines. In particular, Lister<sup>3</sup> has given exact figures for the pH required to give commercially satisfactory exhaustion of both acid and chrome dyes on wool.

In 1948 Ris<sup>4</sup> outlined the work which had been carried out in this field by Messrs. J. R. Geigy AG. of Basle. This work, which had then been carried out only for acid dyes, has now been applied also to chrome dyes.

The object was to supply a great deal of information on the dyeing characteristics of each dye with regard to both its rate of exhaustion and its degree of migration, so that schemes of classification for different purposes could be prepared. This information was given in the form of a graph, since this is the method by which such a wealth of detail can most easily be presented, and it has the great advantage that the dyeing characteristics of a dye can then be seen at a glance. It is also very easy to compare the characteristics of two dyes by simply examining their respective graphs side by side, rather than getting lost in a welter of facts and figures.



It was appreciated at the start that this work would all have to be carried out on one type of material and under the same carefully controlled conditions. The material chosen was worsted yarn, the liquor ratio was 80 : 1, and distilled water was used throughout.

It was also thought necessary to test all dyes at a comparable visual depth of colour rather than at a fixed percentage of dye on weight of fibre. The standard depth 1 ("auxiliary type depth 1") was chosen as standard, since this forms the basis for the assessment of fastness properties of dyes<sup>3</sup>. How inaccurate comparisons based on the percentage depth on weight of fibre would be can readily be seen by comparing the standard depth 1 for four dyes—

Polar Yellow R Conc. ... ..	0.6%
Polar Yellow 2G Conc. ... ..	1.1%
Eriochrome Brown R ... ..	0.9%
Eriochromal Brown G Powder ...	2.0%

Since the actual figures for exhaustion at various temperatures and with various dyeing assistants would have to be established in this case, it was necessary to decide on a method of estimating percentage exhaustion. Two alternative methods were available—

- (1) Indirect—absorptiometric analysis of the dyebath
- (2) Direct—measurement of the depth of colour of the dyeing—
  - (a) By means of a photoelectric colorimeter
  - (b) By comparison with standard dyeings.

Absorptiometric analysis was ruled out because of the possible errors, due mainly to uncertainty as to the degree of dispersion of the dye, which is influenced by temperature, salt concentration, and pH of the dyebath. Other obvious difficulties would arise when testing chrome dyes. A direct means of measurement was therefore required, and the one chosen was comparison with a range of standard dyeings. It was realised that the limit of precision of this method is approx. 5% and that the dyeings must be level to give reliable results.

The standard depth 1 was taken as 100%, and a range of dyeings made at 10% intervals from 10% to 100%.

#### EXHAUSTION CURVES

In order to present the picture clearly and simply, exhaustion curves have been prepared in which the percentage exhaustion is plotted against a combined time-and-temperature axis.

Eight or nine dyebaths are prepared for acid and chrome dyes respectively, each to contain the same amount of dyeing assistant and an amount of dye calculated to give a dyeing of standard depth 1.

Dyeing is begun at 40°C., and the temperature maintained at this value for 15 min.; it is then raised to the boil at the rate of 1°C. per minute, and boiling continued for 1 hr. A dyeing is removed

from one of the dyebaths every 15 min. up to the boil, and then every 30 min. at the boil. The exhaustion curves may be plotted from the results obtained.

As was observed by Goodall<sup>6</sup>, some dyes, particularly the molecularly aggregated Polar or acid milling dyes (e.g. Polar Yellow R and Polar Brilliant Blue GAW), give skittery dyeings when dyed below 80°C. This renders evaluation of the true depth of colour impossible, and it is necessary to "develop" these dyeings by boiling in a fresh bath for 30 min. with sufficient acid to exhaust the dye in question. This gives the normal hue and depth to the dyeing, which can then be satisfactorily compared with the standard dyeings.

The acid levelling dyes are tested in three types of dyebath—

- (1) 10% Glauber's salt crystals plus 2% ammonium sulphate
- (2) 10% Glauber's salt crystals plus 5% acetic acid (30%)
- (3) 10% Glauber's salt crystals plus 5% sulphuric acid (168°Tw.).

For weakly acid and neutral dyeing dyes, No. 3 is omitted as being of little practical value.

For chrome dyes two methods are prescribed—

- (1) Afterchrome method—10% Glauber's salt crystals and 5% acetic acid (30%) exhausted after 105 min. with 2% formic acid (85%)
- (2) Eriochromal or metachrome method—10% Glauber's salt crystals and 4% Metachrome Mordant with and without exhausting with 2% acetic acid (30%) after 105 min.

#### MIGRATION CURVES

For acid dyes the points for plotting the migration curves were obtained by boiling a dyeing of standard depth 1 with an equal weight of undyed material in a blank dyebath, set with identical dyeing assistants to those used in the exhaustion tests. Three tests are made by this method, the times of boiling being 30, 60, and 90 min. respectively. The quantity of dye lost by the dyed material is shown on the upper curve, and the quantity of dye taken up by the lower curve. The amount of dye remaining in the bath is, of course, represented by the difference between percentage loss and percentage uptake.

Similar tests have been carried out on chrome dyes applied by the afterchrome method. In this case it was necessary to test the exhausted but unchromed dyeings for migration, since no migration could be expected from a metachrome dyeing or an afterchrome dyeing after chroming.

#### USE OF GRAPHS OR A SYSTEM OF DYE CLASSIFICATION

Where possible, the dyer will always choose combinations of dyes which possess very similar rates of exhaustion and migration. Most dye manufacturers offer ranges of such dyes, e.g. the Irgalans (Fig. 1 and 2) and the Erio Fast S dyes (Fig. 3 and 4).



## Exhaustion and Migration Curves

Amount of dye in dyebath (% on wt. of yarn) chosen to give Standard Depth 1 under standard conditions of dyeing  
In all cases the dyebath contains 10% Glauber's salt crystals (on wt. of yarn)

— 2% Ammonium sulphate      - - - 5% Acetic acid (30%)      — 5% Sulphuric acid (168°Tw.)

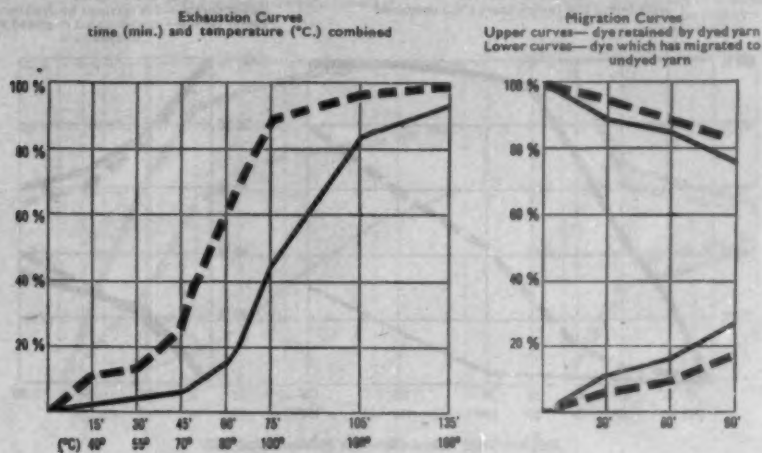


FIG. 1—2.2% Irgalan Grey BL

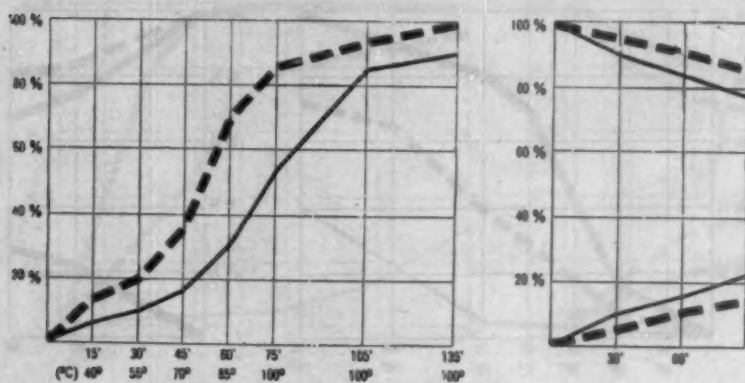


FIG. 2—2.5% Irgalan Brown ZRL

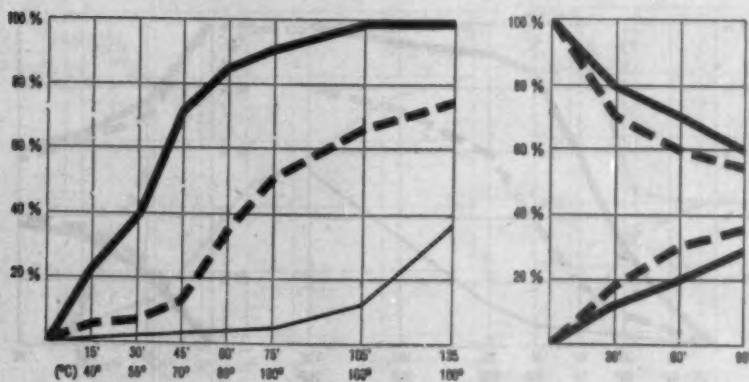


FIG. 3—1.5% Erio Fast Red 2BLS

## Exhaustion and Migration Curves

Amount of dye in dyebath (% on wt. of yarn) chosen to give Standard Depth 1 under standard conditions of dyeing  
In all cases the dyebath contains 10% Glauber's salt crystals (on wt. of yarn)

— 2% Ammonium sulphate    - - - 5% Acetic acid (30%)    — 5% Sulphuric acid (168°Tw.)

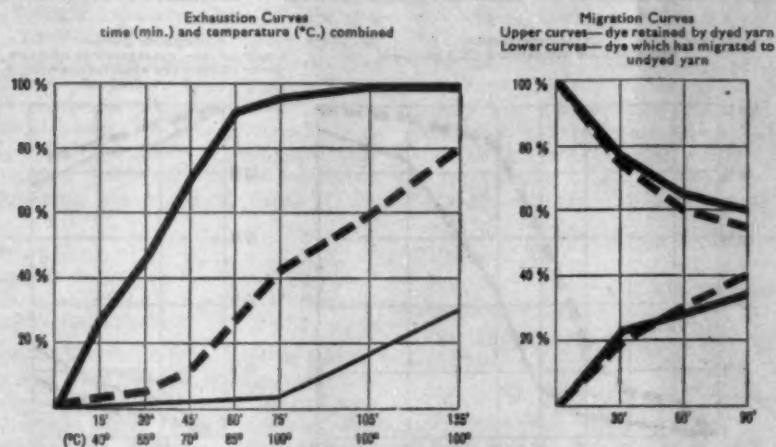


FIG. 4—1.8% Erio Anthracene Brilliant Blue 4GL

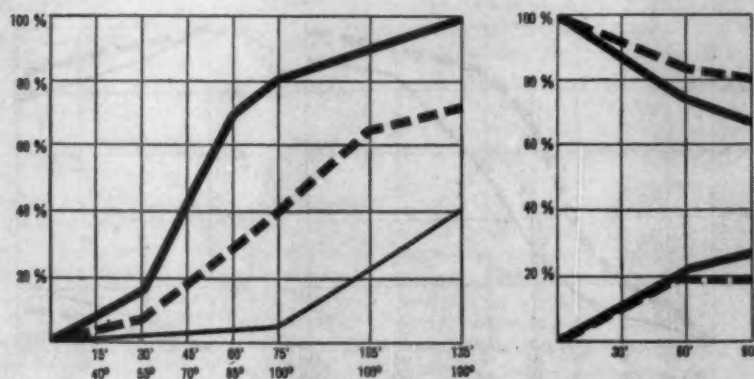


FIG. 5—0% Naphthol Blue Black BC

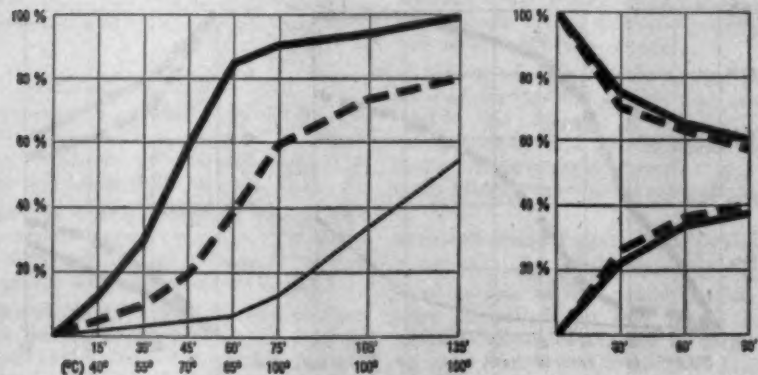


FIG. 6—2.5% Erio Anthracene Rubine R

### Exhaustion and Migration Curves

Amount of dye in dyebath (% on wt. of yarn) chosen to give Standard Depth 1 under standard conditions of dyeing  
In all cases the dyebath contains 10% Glauber's salt crystals (on wt. of yarn)

— 2% Ammonium sulphate    - - - 5% Acetic acid (50%)    — 5% Sulphuric acid (168°Tw.)

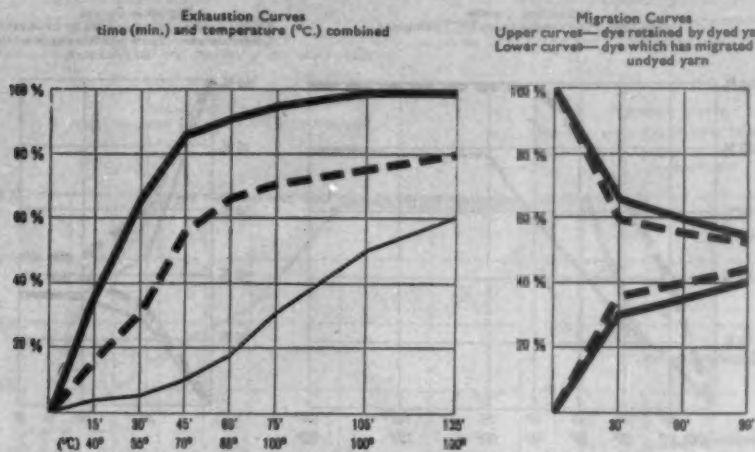


FIG. 7—1.2% Erio Anthracene Cyanine JR

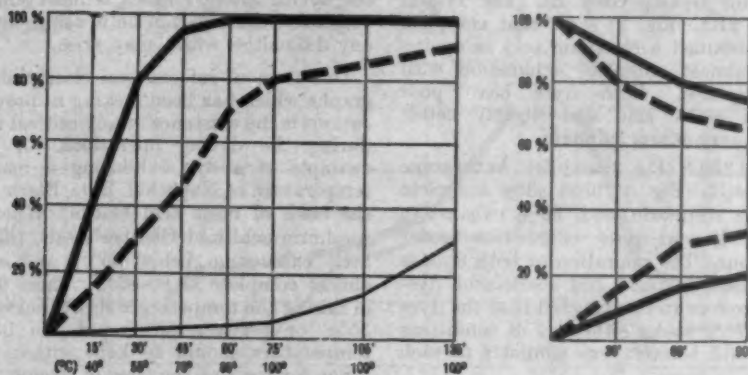


FIG. 8—1.3% Erio Rubine EB

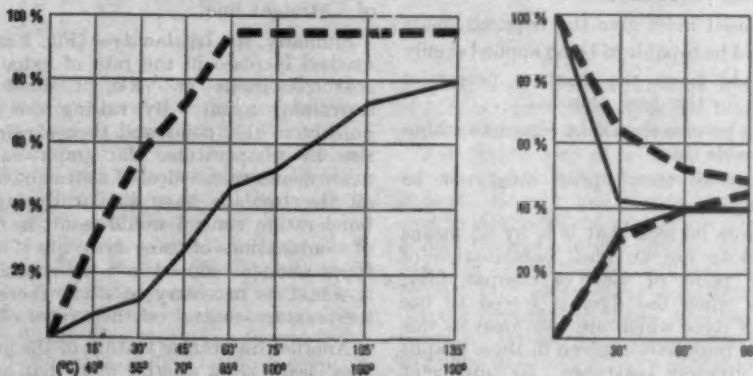


FIG. 9—1.4% Erio Anthracene Brilliant Blue BFF

## Exhaustion and Migration Curves

Amount of dye in dyebath (% on wt. of yarn) chosen to give Standard Depth 1 under standard conditions of dyeing  
In all cases the dyebath contains 10% Glauber's salt crystals (on wt. of yarn)

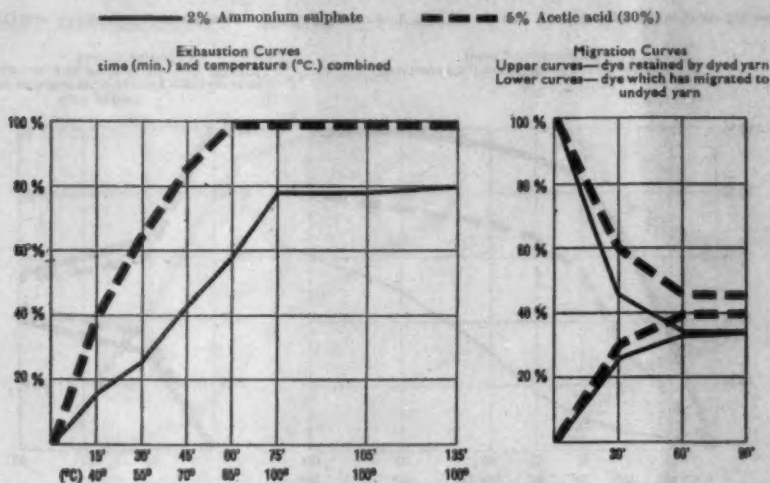


FIG. 10—1% Polar Yellow 5GN

The graphs for Irgalan Grey BL (Fig. 1) and Irgalan Brown 2RL (Fig. 2) show that complete exhaustion is obtained with acetic acid as dyeing assistant and almost complete exhaustion with ammonium sulphate. Both dyes have poor migration with acetic acid and slightly better migration with ammonium sulphate.

Erio Fast Red 2BLS (Fig. 3) and Erio Anthracene Brilliant Blue 4GL (Fig. 4) both show complete exhaustion with sulphuric acid, 80% exhaustion with acetic acid, and poor exhaustion under neutral conditions. The migration of both dyes is good in both sulphuric-acid and acetic-acid dyebaths. It is therefore to be expected that the dyes will be level-dyeing under either set of conditions and that they will behave very similarly to each other.

These graphs will, however, enable the dyer to choose his own combinations, which must also fulfil certain other requirements—

- (1) The dyes used must give the required shade
- (2) They should be capable of being applied evenly
- (3) They should have the fastness properties required for the dyed material
- (4) The dyeing process should be complete within a reasonable time
- (5) Apart from all these, price must not be forgotten.

It will therefore be seen that it is by no means always possible to use an ideal combination of dyes from the point of view of compatibility. However, it is when the dyer is forced to use combinations of dyes which are not ideal in this respect that the information given in these graphs will be of the greatest assistance. By intelligent use of this information, he will be able to work out

the dyeing method which is most suitable for the particular combination he is using, and anticipate any difficulties which may arise.

One item of information clearly shown by the graphs which has been lacking in previous classifications is the existence of any critical temperatures during the dyeing operations. A well known example of a dye exhibiting a marked critical temperature is Naphthol Blue Black BC (Fig. 5), the basis of most acid blacks. When dyed with sulphuric acid and Glauber's salt, this dye shows little exhaustion below 55°C., and exhaustion is almost complete at 80–85°C. There is little point in raising the temperature slowly between 40°C. and 55°C. or between 85°C. and the boil, and the temperature should be kept within the 55–85°C. range for most of the time of dyeing. In this way the rapid rise in exhaustion between these temperatures may be slowed down, so that the exhaustion-time curve will approach much nearer to the ideal of a straight line.

Similarly, the Irgalan dyes (Fig. 1 and 2) show a marked increase in the rate of exhaustion under acid conditions at 70°C. if dyed without a restraining agent. By raising the temperature quickly to this point and then slowing down the rise in temperature, the graph can again be made nearer to the ideal of a straight line. Because all the Irgalans have similar dyeing rates, this temperature control would result in level dyeings of combinations of these dyes; but if dyes of other types were introduced into the combination, then it would be necessary to study the effect of this temperature control on their rates of exhaustion.

Another interesting feature of the graphs is that they clearly show whether more than one method of application is possible with any dye. Certain



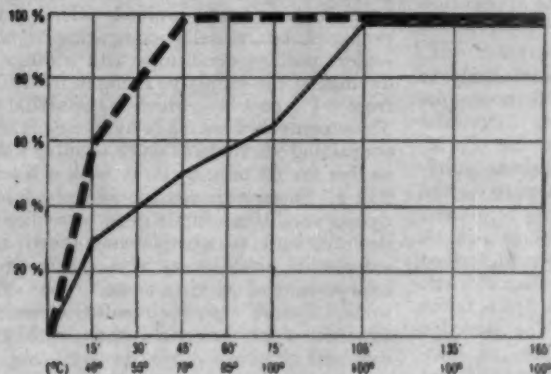
## Exhaustion and Migration Curves

Amount of dye in dyebath (% on wt. of yarn) chosen to give Standard Depth 1 under standard conditions of dyeing  
In all cases the dyebath contains 10% Glauber's salt crystals (on wt. of yarn)

**AFTERCHROME METHOD**  
 --- Dyeing started with 5% acetic acid (30%)  
 — 2% Formic acid (85%) added after 105 min.  
 Potassium dichromate (half the quantity of dye used) added after 135 min.

**METACHROME (ERIOCHROMAL) METHOD**  
 — Dyeing started with 4% Metachrome Mordant  
 --- 2% Acetic acid (30%) added after 105 min.

Exhaustion Curves  
time (min.) and temperature (°C.) combined



Migration Curves  
Upper curves—dye retained by dyed yarn  
Lower curves—dye which has migrated to undyed yarn

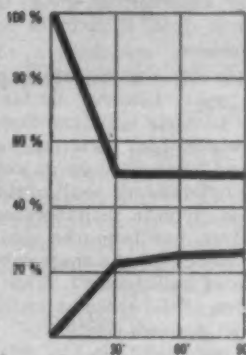


FIG. 11—2% Eriochromal Brown G

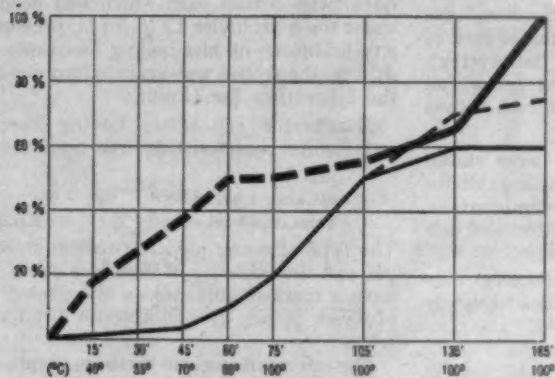


FIG. 12—0.0% Eriochrome Brown R

level-dyeing acid dyes can also be applied under neutral to slightly acid conditions and are therefore very useful as shading agents with Polar, acid milling, and chrome dyes, e.g. Erio Anthracene Rubine R (Fig. 6) and Erio Anthracene Cyanine JR (Fig. 7). Other dyes may be successfully applied from acetic-acid baths and also from sulphuric-acid baths, e.g. Naphthol Blue Black BC (Fig. 5) and Erio Rubine 2B (Fig. 8). Still others may be dyed with the aid of ammonium sulphate and also with acetic acid, e.g. Erio Anthracene Brilliant Blue BFF (Fig. 9) and Polar Yellow 5GN Conc. (Fig. 10). The dual capacity of these dyes may not have been previously realised, but it can now be seen clearly from the

graphs. They can thus be used within wide limits of pH, whereas most dyes are really suitable for application only under one set of conditions.

The graphs also show quite clearly which dyes can be applied by the Eriochromal or metachrome process. Eriochromal Brown G (Fig. 11) may be seen to give excellent exhaustion after only 30 min. boil by the metachrome process, whilst Eriochrome Brown R (Fig. 12) gives only 60% exhaustion after 90 min. boil under these conditions. The afterchrome graphs for these dyes show that Eriochromal Brown G exhausts rapidly, whereas Eriochrome Brown R has a slow rate of absorption. Both dyes have very good migration before chroming, and may therefore be expected to be

level dyeing. This is confirmed by the ease with which both may be applied to piece goods or yarn in practice.

### Direct Cotton Dyes

Since 1884, when Congo Red was first produced, there have become available an ever increasing number of dyes which, owing to their ability to dye unmordanted cotton and other cellulosic fibres from an aqueous dyebath, have received the name of *direct cotton dyes*. The usual instructions for dyeing with such dyes, given in textbooks and pattern cards, suggest that their application is a simple matter, especially as, unlike the application of vat or azoic dyes, it involves no complicated chemical reactions.

Dyeing with direct cotton dyes, particularly in combination, may, however, be far from simple. This is due to their widely differing individual behaviour, which has been stressed by C. M. Whittaker and his colleagues in numerous publications. The outstanding result of the work carried out on viscose rayon in the laboratories of Messrs. Courtaulds Ltd. has been the establishment by Boulton and Reading<sup>7</sup> of a characteristic described as "the time of half-dyeing". This characteristic is an indication of the speed at which dye is taken up under well defined conditions. The recorded results vary from 0.72 min. to 280 min., a four-hundredfold variation. It was then suggested that dyes possessing a similar time of half-dyeing would work better in combination than dyes for which the values differ widely. However, Boulton<sup>8</sup> has stated that, in spite of the importance of rate of dyeing (which is related to the time of half-dyeing), its measurement alone is insufficient for a full understanding of the behaviour of direct cotton dyes.

Lemin, Vickers, and Vickerstaff<sup>9</sup> have stated that rate of dyeing alone is not a reliable guide for predicting the compatibility of dyes in combination, and they consider that rate of migration and salt controllability are of greater importance.

The committee set up by the Society concluded<sup>10</sup> that dyeing behaviour can be adequately defined by the following properties—

- (1) Migration or levelling power
- (2) Salt controllability
- (3) Influence of temperature on exhaustion
- (4) Influence of liquor ratio on exhaustion.

Test were provided for only (1) and (2), (3) and (4) being covered by a statement.

On this basis it was recommended that direct cotton dyes be classified into three groups, as follows—

**CLASS A**—Dyes which are self-levelling, i.e. dyes of good migration.

**CLASS B**—Dyes which are not self-levelling but which can be controlled by regulated additions of salt to give a level result. These are defined as being "salt-controllable".

**CLASS C**—Dyes which are not self-levelling and are highly sensitive to salt. The exhaustion of

these dyes cannot be adequately controlled by additions of salt alone, and therefore additional control by temperature is required. These are referred to as "temperature-controllable".

This classification has the great advantage that it can be worked out on the basis of only two tests, and it therefore affords a ready means of assessing the dyeing properties of direct cotton dyes without necessitating a great deal of work.

The contribution of the Geigy Co. Ltd. to the classification of direct cotton dyes was made in June 1944 and, again, was in the form of a graphical representation<sup>11</sup>, from which a classification has been evolved. The graphs were prepared by visually comparing dyeings made under specified conditions with a range of control dyeings of the same dye rising in intervals of 0.1% from 0.1% to 1.3%, which is the actual scale used. These controls were made by dyeing from dyebaths containing ten times as much Glauber's salt crystals as dye for 60 min. at 95°C. with a liquor ratio of 20 : 1. These were considered to be fairly average dyeing conditions, but it must be realised that they do not lead to complete or even satisfactory exhaustion with every dye. This provides the explanation of why, in some graphs, variation in some factors gives results showing higher exhaustion or dye yield than with the control dyeings.

The material used throughout these tests was 2/40s Egyptian gassed super Sakel 18-turns right-twist cotton yarn which had been boiled in water for 6 hr. under 10 lb./sq.in. pressure without any additions of kier-boiling assistants. Prior to dyeing, the cotton was again boiled out in water in the laboratory for 15 min.

Manchester tap-water, having the following important characteristics, was used throughout—

pH ... ..	7.0
pH after 1 hr. at 95°C. ...	7.8
Total dissolved solids ...	39 p.p.m.

The type of water used is stressed, since both the pH and the quantity of dissolved solids in a water have a marked influence on the dyeing behaviour of direct cotton dyes in absence of added electrolytes.

The information given by these graphs covers the following factors—

(1) Rate of exhaustion	} Characteristic properties of dyes*
(2) Degree of migration	
(3) Time of dyeing	} External factors capable of control
(4) Temperature of dyeing	
(5) Concentration of Glauber's salt	
(6) Liquor ratio	

#### 1. RATE OF EXHAUSTION

In this test 1% dyeings were made from a dyebath containing 10% Glauber's salt crystals (both on weight of yarn), liquor ratio 20 : 1, for 10 min. at 95°C. The yarn was then squeezed

\* In these graphs these properties refer to dyes plus 10% Glauber's salt crystals.

thoroughly, the liquor being returned to the bath, a second hank entered, and the process repeated until all the dye had been exhausted from the bath.

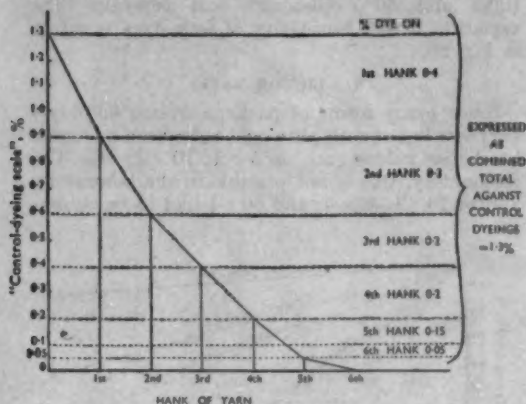


FIG. 13—Rate of Exhaustion of Diphenyl Brown MG

The method by which such curves are built up from the depth of colour of each hank is shown in Fig. 13. The variation in absorption between Diphenyl Brown MG and Diphenyl Brown BVV, which are typical examples of dyes which exhaust slowly and rapidly respectively, is shown in Fig. 14.

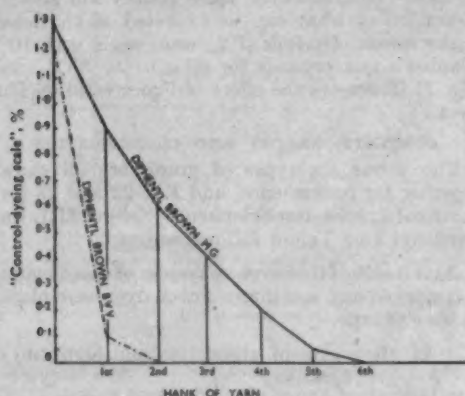


FIG. 14—Variation in Rate of Exhaustion

The value of this test lies mainly in assessing the initial "strike" or speed of dyeing, and in comparing this property in dyes to be used together.

## 2. MIGRATION

Dyeings (2%) were made at a liquor ratio of 20 : 1 for 60 min. at 95°C. with 10% Glauber's salt crystals. Equal weights of dyed and undyed material were then treated for 15, 30, 45, 60, 90, 120, and 240 min. respectively at 95°C. in a blank bath containing 10% Glauber's salt crystals (calculated on the total weight of yarn), at a liquor ratio of 20 : 1. The amount of dye taken up by the undyed fibre (visual assessment) is plotted, and, to complete the picture, the amount of dye remaining on the original hank and that remaining in the dyebath are given for the 240-min. test.

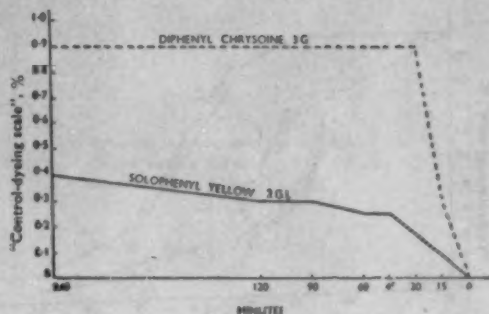


FIG. 15—Migration

The difference in migration between Diphenyl Chrysoine 3G and Solophenyl Yellow 2GL, dyes with excellent and moderate migration respectively, is shown in Fig. 15.

## 3. TIME OF DYEING

Dyeings (1%) were made at 95°C. and a liquor ratio of 20 : 1 without Glauber's salt for 15, 30, 45, 60, 75, and 90 min. This dye liquor corresponds to most dye liquors used in practice, to which Glauber's salt is usually added at a later stage.

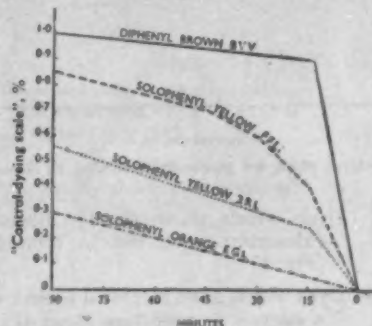


FIG. 16—Effect of Time on Dyeing

Fig. 16 shows the variation in exhaustion of four direct cotton dyes.

## 4. TEMPERATURE OF DYEING

Dyeings were made for 60 min. in a 20 : 1 liquor containing 10% Glauber's salt crystals at 20°, 30°, 40°, 50°, 60°, 70°, 80°, 90°, and 95°C.

From a study of the effect of temperature it can be seen that direct cotton dyes roughly fall into three classes, as shown in Fig. 17—19—

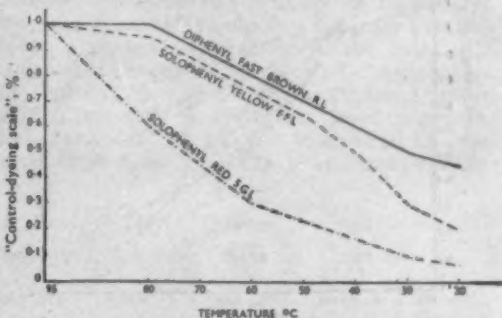


FIG. 17—Dyes which show Steady Increase in Substantivity with Increase in Temperature

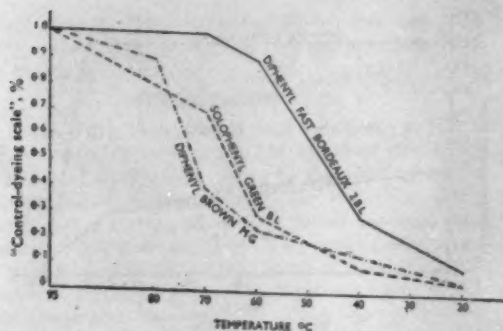


FIG. 18—Dyes which show a Critical Period within a Narrow Temperature Range

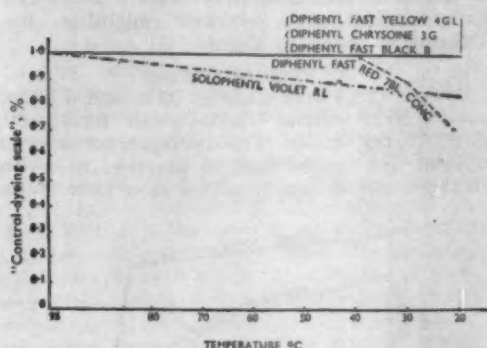


FIG. 19—Dyes which are practically unaffected by Temperature

- (1) Dyes which show steady increase in exhaustion with rise in temperature (Fig. 17)
- (2) Dyes which have a critical period within a narrow temperature range (Fig. 18)
- (3) Dyes which are practically unaffected by temperature (Fig. 19).

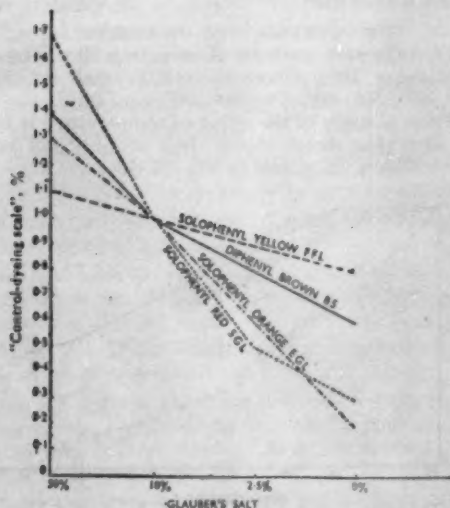


FIG. 20—Effect of Glauber's Salt

## 5. CONCENTRATION OF GLAUBER'S SALT

Dyeings (1%) were made at 95°C. for 60 min. at a liquor ratio of 20 : 1 with the addition of 0, 2.5%, 10%, and 50% Glauber's salt crystals. The variation in salt sensitivity of four dyes is shown in Fig. 20.

## 6. LIQUOR RATIO

Since many forms of package dyeing employ a very low liquor ratio, it would have been advisable to choose values such as 5 : 1, 10 : 1, etc. Unfortunately, this is not possible in the laboratory, and so 20 : 1, 40 : 1, and 60 : 1 had to be chosen.

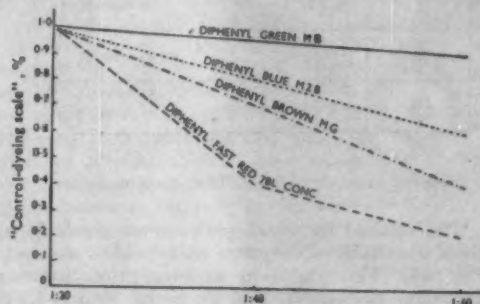


FIG. 21—Effect of Liquor Ratio

In most cases, however, these results will give an indication of what can be expected at the lower liquor ratios. Dyeings (1%) were made with 10% Glauber's salt crystals for 60 min. at 95°C., and Fig. 21 illustrates the effect of liquor ratio on four dyes.

## COMPLETE GRAPHS AND CLASSIFICATION

The above six types of graph are all shown together for convenience, and Fig. 22 and 23 give the final graphs for Solophenyl Yellow 2RL and Diphenyl Fast Yellow RL respectively.

As a result of this work, a system of classification was worked out, and direct cotton dyes were placed in four groups—

- A—High rate of absorption and high rate of migration
- B—Low rate of absorption and low rate of migration
- C—High rate of absorption and low rate of migration
- D—Low rate of absorption and high rate of migration.

Each group was then subdivided into four subgroups, as follows—

- (1) Uncontrollable by temperature or salt
- (2) Controllable by salt
- (3) Controllable by temperature
- (4) Controllable by salt and temperature.

This classification thus differs from the Society's<sup>10</sup> in being somewhat more detailed, and in particular, it takes into account the rate of strike of a dye in addition to its rate of migration.



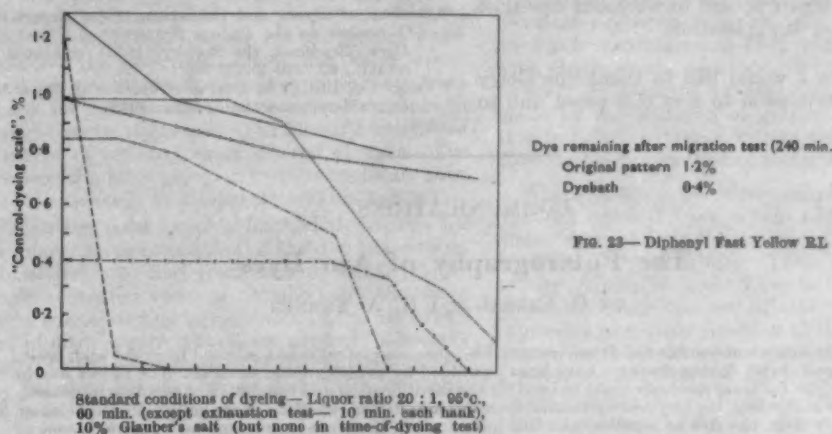
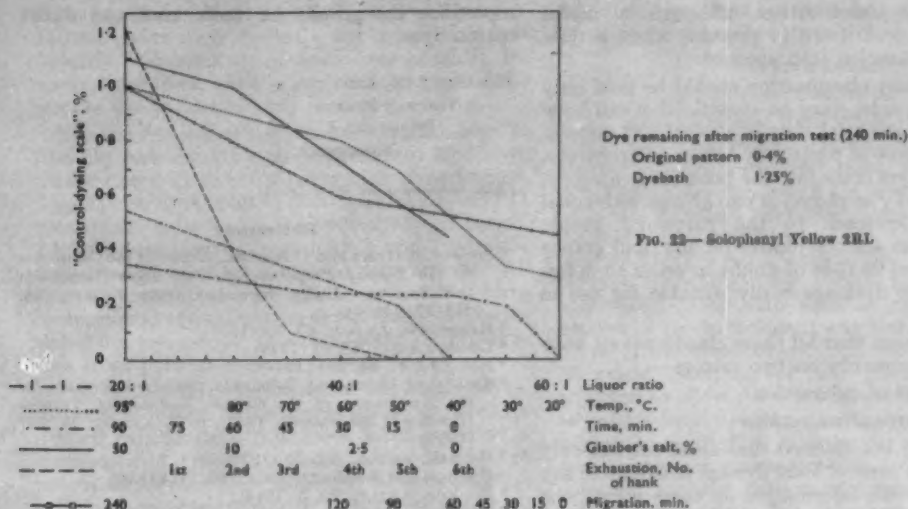


Fig. 22 and 23—Complete Graphs for two Direct Cotton Dyes  
(the abscissas are to be read from right to left except in the case of the exhaustion test)

Even in the Society's classification, however, rate of dyeing comes indirectly into consideration. Where migration cannot be relied on to produce level results, control by salt (Class B) or temperature (Class C) is necessary, both of which depend on a slowing down of the rate of exhaustion. There are, however, other points in favour of including rate of exhaustion. The true test of any classification is its successful application in practice, and a combination of Diphenyl Fast Red 7BL, Polyphenyl Orange SP, and Diphenyl Fast Black B provides a typical example. The properties of these dyes are given in the table.

These three dyes, on account of their good migration properties, are listed in Class A by the Society's method, and should therefore dye satisfactorily in combination. The Geigy classification, however, shows the slower exhaustion and different salt sensitivity of the red. In practice, it is found that this results in a tendency for there to be a predominance of red in the bath, with consequent trouble in matching off. Replacement of Diphenyl Fast Red 7BL by Diphenyl Brown BVV (high rate of absorption, good migration, Geigy classification A 1) has been found to overcome these difficulties. This is an example where

	Geigy Class	Migration	Exhaustion		Control by	
			10% Salt	No Salt	Temp.	Salt
Diphenyl Fast Red 7BL	D 2	Excellent	Very slow	Very slow	None	Excellent
Polyphenyl Orange SP	A 3	Very good	Very quick	Quick	Good	Poor
Diphenyl Fast Black B	A 1	Very good	Very quick	Quick	None	Poor

the Society's classification, although a useful guide, may break down in practice, since it does not take exhaustion into account.

However, any classification should be used only as a general guide, since no classification can hope to give such essential details as critical temperatures and degree of control by salt or temperature. Also, many dyes come into the borderline category, and could really be placed in two groups with equal accuracy. Reference to the particular graph, however, gives a much clearer picture, and graphs should be used in case of doubt in order to determine whether dyes are really suitable for use in combination.

It will be seen that all these classifications have been based primarily on two factors—

- (1) Rate of exhaustion
- (2) Degree of migration.

Whilst it is not claimed that these are the only factors which control level dyeing, it is true to say that, armed with information on these points, the dyer is in a much better position to select his dyes for use in combination, and to work out the most suitable method of application.

\* \* \*

In conclusion I would like to thank the Geigy Co. Ltd. for permission to give this paper and to

reproduce the graphs for both wool and direct cotton dyes.

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(MS. received 18th May 1955)

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## COMMUNICATIONS

### The Polarography of Azo Dyes

J. DE O. CABRAL and H. A. TURNER

Twenty-one water-soluble azo dyes—mono-, bis-, tris-, and tetrakis-azo, selected from the acid, basic, mordant, and direct dyeing classes—have been examined by polarographic methods. The object was to determine how far these methods could be used for the identification and estimation of azo dyes in general. With a few exceptions, the half-wave potential corresponding to the reduction of azo groups does not change very greatly from one dye to another, and this quantity has therefore little value as a general means of identification. When the correct experimental conditions have been established, the polarographic method lends itself to the accurate estimation of all the dyes that have been studied.

#### INTRODUCTION

From time to time, single dyes or small groups of azo <sup>1–3</sup>, nitro <sup>4,5</sup>, quinonoid <sup>6–8</sup>, and other chemical varieties of dyes <sup>7</sup> have been examined with the polarograph, either to obtain information about reduction mechanisms or to identify the products of reduction obtained under different conditions. But, in spite of the very wide use of polarographic examination for quantitative analytical purposes, little has been done to show how it can be employed for the identification or estimation of dyes. This is especially remarkable since there are so many compounds in this class of organic substances which should, *a priori*, qualify for application of the method. To be of interest to the analyst, there should be studies of each of the important chemical classes, based on a reasonably large number of representative dyes for each class.

The water-soluble azo dyes seem to be particularly worthy of examination. The chemical class

is a large one and includes members from a number of application classes—acid, mordant, basic, direct cotton, soluble acetate-rayon, etc. In the volumetric analysis of azo dyes in general, reduction methods, such as the titanous salt methods of E. Knecht and E. Hibbert <sup>9</sup>, can be applied very widely, so that initial standardisation of dye solutions is easy. As between one azo dye and another, the total molecular constitution can vary greatly, with a consequent change in properties such as solubility and tendency towards molecular aggregation in solution. This poses many interesting problems in the attempt to prescribe experimental conditions which will not call for elaborate modification as different dyes come to be examined.

M. Shikata and I. Tachi <sup>10</sup> were among the first in this field, but their work was confined to the examination of three simple compounds none of which can be regarded as a genuine dye. N. H.

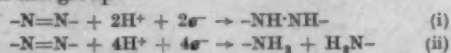
Hoang<sup>1</sup>, G. A. Gilbert and E. K. Rideal<sup>11</sup>, and A. Pittoni<sup>2</sup> have each studied a few simple azo dyes (usually sulphonated monoazo compounds) for various purposes, but the analytical interest of the studies was incidental only.

The chief object of the present work has been to find out how readily dyes could be (a) identified, (b) estimated by direct polarographic examination. Twenty-one dyes in all were studied, comprising 11 monoazo (7 aminoazo and 4 hydroxyazo), 7 bisazo, 2 trisazo (one derived from J acid), and 1 tetrakisazo. Two of the dyes contained nitro groups. All were obtained in as pure a form as possible, some by fractional crystallisation or fractional precipitation from commercial products, some by preparation from purified intermediates.

For successful identification of single dyes, cathodic reduction of the azo group under carefully defined experimental conditions must occur at a characteristic mean voltage (the half-wave potential) for each dye. Although differences in the half-wave potential from dye to dye were observed, they were not always very large, and did not appear to bear any simple relation to important features in the molecular constitution. At the present stage, therefore, the determination of this value under standard conditions does not promise any great success for general identification purposes, though it might serve, on occasion, to identify individual members of selected small groups of dyes. The presence of a nitro group in the dye molecule gave rise, as expected, to a separate and distinct wave.

When the polarographic method is invoked for the quantitative estimation of the dye in solution, it is desirable to find conditions in which (a) the simple reduction wave is obtained, (b) the wave height corresponding to reduction of the azo group (and of nitro groups if these are present) is linearly related to the concentration of dye in the solution. The relation between these quantities depends, *inter alia*, upon the diffusion coefficient of the dye particles, and this, in turn, upon the extent of molecular aggregation. It is therefore desirable to work over a concentration range in which the dye is molecularly dispersed, and, should it be sparingly soluble, to add to water suitable solvents or other agents to assist dispersion. Although it would be an advantage if standard conditions applicable to all dyes could be prescribed, this was not found to be possible. Nevertheless, by simple and systematic variation of the composition of the solution with respect to solvent, buffers, and, as required, the presence of a peak suppressor, a useful range of concentration has been found for each dye, within the limits of which the linear relation was found to hold.

There are two basic alternatives in the reduction of the azo group—



M. Shikata and I. Tachi<sup>10</sup> have obtained results which suggest that (i) applies, while G. A. Gilbert and E. K. Rideal<sup>11</sup> have found that four electrons are required for each azo group in the cathodic reduction of an isomer of Orange G. In the present

selection, some dyes appear to be reduced according to (i) and some according to (ii).

## EXPERIMENTAL

### Apparatus and General Procedure

All measurements were made with a photographically recording polarograph (Cambridge Instrument Co.), the cell being of the pattern designed by the makers of the instrument for use with an external reference electrode (saturated calomel). Its capacity was 2 ml. Purified nitrogen (British Oxygen Co., "oxygen free") was bubbled through the solution for 10 min. before a reading was made. Jets were used as supplied by the makers of the instrument, and were found to give drops of the specified size and rate of formation. Electrical damping of the galvanometer was adjusted to allow the trace of the wave to occupy as great a height on the chart as possible, without having to restrict it in order to allow room for oscillations of considerable amplitude. The damping was not carried so far as to cause distortion of the wave. The galvanometer sensitivity and the range of applied voltage were each adjusted to values which would give a fully developed wave, on which measurements of height could be taken with the requisite accuracy. When maxima were formed, an attempt to suppress them was first made by the addition of gelatin to the solution. If this failed, suppression was achieved by using aqueous alcohol instead of water as the solvent.

Where possible, i.e. where coordination between dye and metal did not occur, additional measurements were made in the presence of a suitable pilot ion ( $\text{Cd}^{2+}$ ,  $\text{Tl}^+$ , or  $\text{Ni}^{2+}$ ). These ions are referred to by Kolthoff and Lingane<sup>12</sup> as "internal standards", but the use of this term is liable to cause this particular function of the accompanying ions to be confused with other purposes for which a reference ion may be used. The height of the waves was determined from the traces by the three-tangent method<sup>13</sup> (Fig. 1), since in this way the correction for residual current is automatically introduced. The graduations on the voltage scale of the polarogram each correspond to 0.1 v., and values for the half-wave potential ( $E_1$ ) were estimated to 0.01 v. The figure of merit of the galvanometer had been separately determined, and the wave height ( $h$  mm.) could be transformed into the diffusion current ( $i_d$  microamp.) by the equation—

$$i_d = 4.64 \times 10^{-3} \frac{h}{s}$$

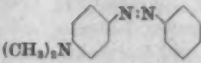
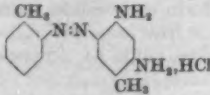
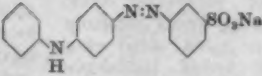
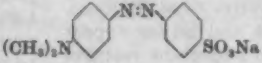
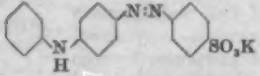
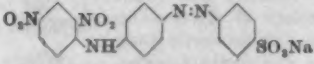
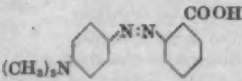
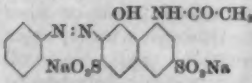
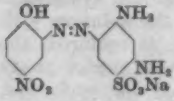
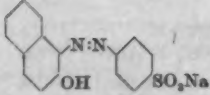
where  $s$  is the sensitivity.

For each concentration of the dye solution a polarogram was obtained at the most suitable sensitivity, and the wave height on each was reduced to a common sensitivity before plotting against concentration. Similarly, the wave heights of the accompanying pilot ion at a standard concentration were reduced to the same sensitivity as that chosen as common for the dye itself, and the ratio—

$$\frac{h}{h'} = \frac{\text{Height of dye wave}}{\text{Height of pilot ion wave}}$$

was also plotted against dye concentration.

TABLE I  
Summary of Experimental Data

Dye	Maker	C.I. No.	Constitution	Method of Purification*
MONOAZO Butter Yellow	Fran	10		Xn. C <sub>6</sub> H <sub>5</sub> OH
Chrysoidine R (basic)	INAC	60		Xn. H <sub>2</sub> O
Metanil Yellow (acid)	ICI	138		Xn. aq. C <sub>6</sub> H <sub>5</sub> OH
Methyl Orange (acid)	Fran	142		Xn. H <sub>2</sub> O
Orange IV (acid)	—	143		P.I., Xn. H <sub>2</sub> O
Azo Yellow FFN (acid)	ICI	147		Xn. H <sub>2</sub> O
Methyl Red (acid)	Fran	211		Xn. C <sub>6</sub> H <sub>5</sub> OH
Amidonaphthol Red G (acid)	—	31		P.I., Xn. H <sub>2</sub> O
Eriochrome Brown R (mordant)	INAC	98		Xn. H <sub>2</sub> O
Orange II (acid)	—	151		P.I., Xn. C <sub>6</sub> H <sub>5</sub> OH

\* P.I. = From purified intermediates  
Xn. = Crystallization from



TABLE I  
 Summary of Experimental Data

Group reduced	$E_1$ (v.) at pH				Formation of Maximum	Range of Linearity $h-C$ (g./litre)	Pilot Ion	For Calibration Curve † at pH	$\frac{h}{C}$	$\frac{h}{h'}$	$\frac{h}{C}$	$\frac{h}{h'}$	Remarks
	4-65	4-75	9-15	9-25									
N:N	—	—	-0.65	—	None. $C_2H_5OH$ to improve solubility	0-04-0-11	$Tl^+$	9-15	1/7	423.6	20-0	—	—
N:N	—	-0.30	-0.72	—	None. $C_2H_5OH$ at pH 9-15 to improve solubility	—	$Cd^{2+}$ (pH 4-75)	—	—	—	—	—	—
						0-08-0-26	$Ni^{2+}$ (pH 9-15)	9-15	1/30	179.9	14-1	—	—
N:N	-0.80	—	-0.58	—	None. $C_2H_5OH$ at pH 9-15 to improve solubility	—	$Cd^{2+}$ (pH 4-65)	—	—	—	—	—	—
						0-08-0-24	$Cd^{2+}$ (pH 9-15)	9-15	1/20	126.8	4-6	—	—
N:N	—	-0.23	—	-0.60	None	—	$Cd^{2+}$ (pH 4-75)	—	—	—	—	—	—
						0-04-0-12	$Cd^{2+}$ (pH 9-25)	9-25	1/10	207.5	6-60	—	—
N:N	—	-0.27	-0.55	-0.56	None. $C_2H_5OH$ to improve solubility	—	—	—	—	—	—	—	—
						0-05-0-20	$Cd^{2+}$	9-25	1/20	117.6	5-1	—	—
N:N	—	-0.25	-0.48	-0.52	None See Remarks	—	—	—	—	—	—	—	Gelatin improved definition of waves
						0-018-0-10	—	9-15	1/5	507.1	—	—	In aq. soln. (pH 9-25) aggregation marked, $h-C$ curve not linear
$NO_2$	—	-0.44	-0.77	-0.71		—	—	—	—	—	—	—	In alcohol soln. (pH 9-15) curve linear
						0-02-0-10	—	9-15	1/5	—	—	—	—
N:N	-0.22	—	-0.51	—	pH 4-65 Suppressed by gelatin pH 9-15 None. Solubility improved by $C_2H_5OH$	—	$Cd^{2+}$	—	—	—	—	—	—
						0-05-0-25	$Cd^{2+}$	9-15	1/50	187.8	7-4	—	—
N:N	—	-0.42	—	-0.64	None	—	$Cd^{2+}$ (pH 4-75)	—	—	—	—	—	—
						0-04-0-32	$Cd^{2+}$ (pH 9-25)	9-25	1/20	151.6	5-7	—	—
N:N	-0.35	—	-0.61	—	None. $C_2H_5OH$ required to prevent pptn. at pH 4-65 and 9-15	—	—	—	—	—	—	—	Complex formation with $Ni^{2+}$
						0-04-0-20	—	9-15	1/20	173-1	—	—	Suppression of $Ni^{2+}$ wave
$NO_2$	-0.66	—	-0.95	—		—	—	—	—	—	—	—	Waves for N:N and $NO_2$ each increased in height; $E_1$ more negative
						0-04-0-20	—	9-15	1/20	262.5	—	—	—
N:N	—	-0.33	—	-0.61	None	—	—	—	—	—	—	—	$E_1 = -0.72$ in 0.1N-KCl (pH approx. 7.0)
						0-03-0-25	$Tl^+$	~7-0	1/20	237.9	13-2	—	—

† The limits of linearity in the calibration curves are those actually observed in determinations. All these curves, if produced, pass through the origin, within the limits of experimental error.

‡  $\lambda$  = Wave height (mm.)

$h'$  = Wave height (mm.), pilot ion

$C$  = Concn. of dye (g./litre)

TABLE I  
Summary of Experimental Data

Dye	Maker	C.I. No.	Constitution	Method of Purification*
Naphthalene Scarlet 4R (acid)	ICI	185		Xn. H <sub>2</sub> O
Disazo Naphthalene Leather Brown A (acid)	ICI	234		Xn. H <sub>2</sub> O
Naphthalene Leather Brown AD (acid)	ICI	235		Xn. H <sub>2</sub> O
Bismarck Brown (basic)	INAC	332		Xn. H <sub>2</sub> O
Congo Red (direct)	Fran	370		Fractional pptn. of free acid from H <sub>2</sub> O
Benzopurpurin 10B (direct)	—	495		P.I., Xn. H <sub>2</sub> O
Chlorazol Sky Blue FF (direct)	—	518		P.I., Mills and Robinson's purification
Diamine Sky Blue A (direct)	—	520		P.I., Mills and Robinson's purification
TRISAZO Formic Black C (direct)	INAC	581		Xn. C <sub>2</sub> H <sub>4</sub> OH
Durazol Blue 2R (direct)	ICI	533		Xn. H <sub>2</sub> O
TETRAKIBAZO Viscose Black G... (direct)	INAC	—		Xn. H <sub>2</sub> O

\* P.I. = From purified intermediates

Xn. = Crystallization from

TABLE I  
 Summary of Experimental Data

Group reduced	$E_{\frac{1}{2}}$ (v.) at pH				Formation of Maximum	Range of Linearity $h-C$ (g./litre)	Pilot Ion	For Calibration Curve $\dagger$ at pH Sensitivity	$\frac{h}{C} \dagger$	$\frac{h}{h'} \dagger$	Remarks
	4.65	4.75	9.15	9.25							
N:N	—	-0.30	—	-0.66	Maxima at high and low pH, suppressed by gelatin	0.08-0.20	Cd <sup>2+</sup> (pH 4.75) Cd <sup>2+</sup> (pH 9.25)	— — 0.25 1/20 192.0	— — 5.8	—	—
N:N	—	-0.29	-0.55 <sup>a</sup>	-0.61 <sup>b</sup>	Maxima suppressed by gelatin	— 0.1-0.4	— Cd <sup>2+</sup>	— 0.15 1/20 111.9	— 5.7	—	<sup>a</sup> In presence of C <sub>2</sub> H <sub>5</sub> OH, first wave <sup>b</sup> In absence of C <sub>2</sub> H <sub>5</sub> OH, first wave
N:N	—	-0.26	-0.53	-0.63	Maxima suppressed by C <sub>2</sub> H <sub>5</sub> OH but not by gelatin	0.1-0.3	Cd <sup>2+</sup>	0.15 1/10 72.5	3.6	—	—
N:N	-0.39	—	-0.71	—	C <sub>2</sub> H <sub>5</sub> OH to increase solubility. Gelatin to suppress maxima	0.03-0.2	Ni <sup>2+</sup>	0.15 1/20 220.5	11.4	—	—
N:N	— <sup>c</sup>	— <sup>c</sup>	-0.66	-0.65	C <sub>2</sub> H <sub>5</sub> OH required to extend solubility range	0.09-0.25	Cd <sup>2+</sup>	0.25 1/10 140.9	4.5	—	<sup>c</sup> Tautomeric change in acid soln., no well defined waves
N:N	— <sup>d</sup>	-0.27 <sup>d</sup>	-0.60	—	C <sub>2</sub> H <sub>5</sub> OH to extend solubility range	0.02-0.08	Tl <sup>+</sup>	0.15 1/5 290.8	27.3	—	<sup>d</sup> No well defined waves
N:N	—	-0.33	—	-0.64	None	0.16-0.4	Cd <sup>2+</sup>	0.25 1/20 107.2	3.9	—	—
N:N	—	-0.44 <sup>e</sup>	—	-0.77	None	0.07-0.32	Tl <sup>+</sup>	0.25 1/20 129.9	6.7	—	<sup>e</sup> Not well defined
N:N	—	-0.28	-0.67	-0.68	C <sub>2</sub> H <sub>5</sub> OH improves solubility	0.08-0.24 0.07-0.33	— —	0.25 1/10 179.4 0.15 1/10 134.4	— —	—	Presence of alcohol (pH 9.15) increases range of linearity After max. concn. great deviations from linearity
N:N	—	-0.35	—	-0.70	None	0.08-0.40	Tl <sup>+</sup>	0.25 1/20 86.8	4.6	—	—
N:N	—	—	—	-0.68	None	0.08-0.25	Ni <sup>2+</sup>	0.25 1/30 95.3	2.5	—	Marked departure from linearity after max. concn. is exceeded

$\dagger$  The limits of linearity in the calibration curves are those actually observed in determinations. All these curves, if produced, pass through the origin, within the limits of experimental error.

$\dagger h$  = Wave height (mm.)

$h'$  = Wave height (mm.), pilot ion

$C$  = Concn. of dye (g./litre)

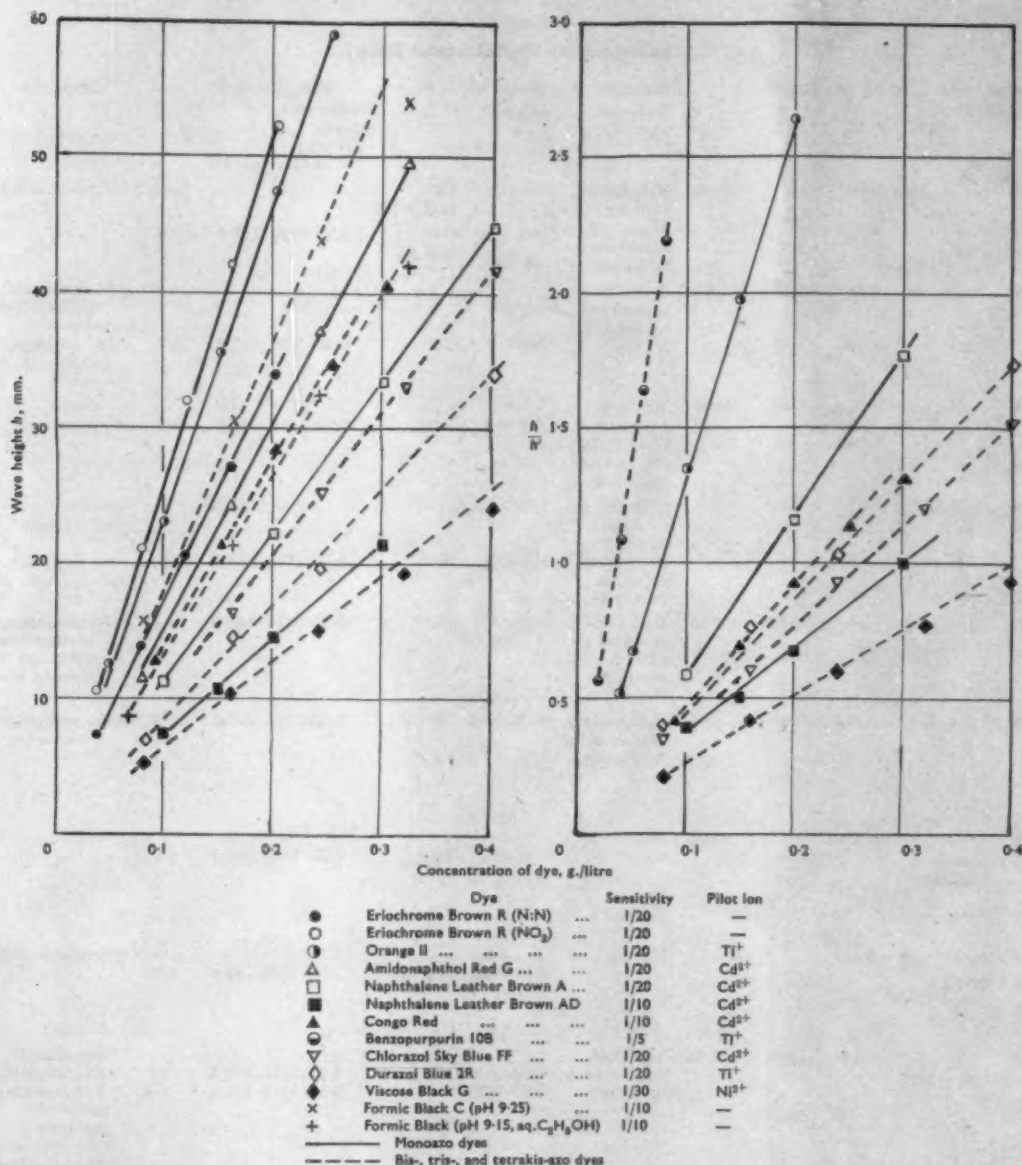


FIG. 2.—Examples of Calibration Curves

### Experimental Solutions

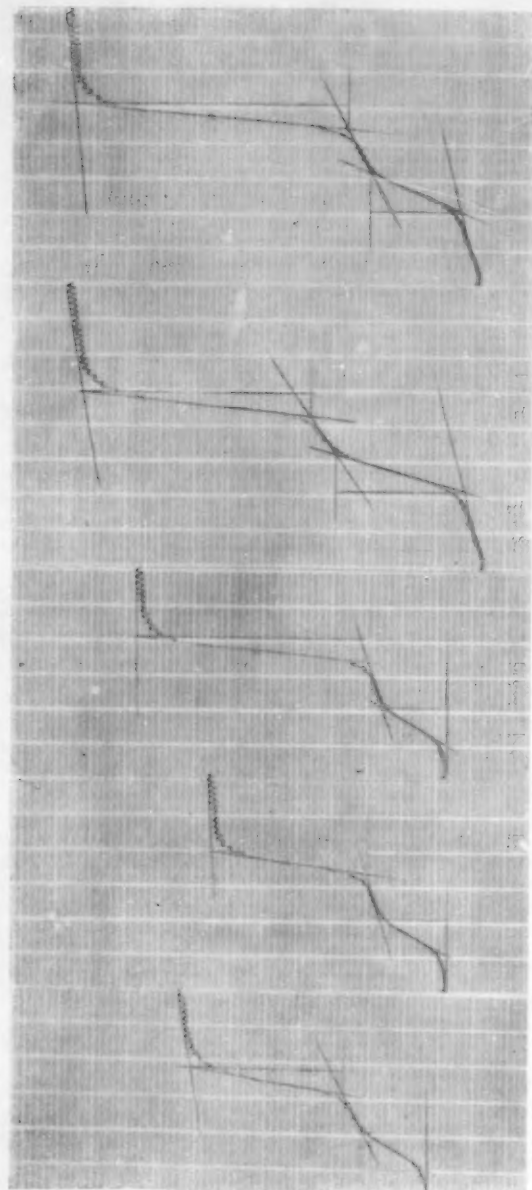
Six solutions were prepared, all from AnalaR reagents—

A	Base electrolyte	0.5 M-KCl
B	Base electrolyte and peak suppressor	0.5 M-KCl in 2% gelatin
C	Acid buffer (pH 4.75)	2 M-CH <sub>3</sub> -COOH + 2 M-CH <sub>3</sub> -COONa
D	Alkaline buffer (pH 9.25)	2 M-NH <sub>4</sub> OH + 2 M-NH <sub>4</sub> Cl
E	Source of pilot ion	8.93 × 10 <sup>-4</sup> M-TiCl <sub>3</sub>
F	Source of pilot ion	8.95 × 10 <sup>-3</sup> M-CdSO <sub>4</sub>
G	Source of pilot ion	7.29 × 10 <sup>-3</sup> M-NiSO <sub>4</sub>

Stock solutions of the dyes were prepared in distilled water or in 70% aqueous alcohol at concentrations between 1.0 and 2.5 g./litre.

In preliminary experiments, solutions of the dye in acid, neutral, and alkaline solutions, along with the base electrolyte and the appropriate pilot ions, were prepared and polarograms taken. From these it was decided—(a) whether the presence of gelatin was required, (b) what adjustments were necessary to give the desired pH in the solution, and (c) the most suitable pilot ion. After the best composition for the medium had been found, a series of solutions were prepared with this medium,





(a)

(b)

(c)

(d)

Composition of Solutions (ml.)				
(a)	(b)	(c)	(d)	(e)
Stock dye (1 g./litre) ...	2	3	4	5
70% aqueous alcohol ...	25	25	25	25
Solution A ...	5	5	5	5
Solution D ...	5	5	5	5
Water to ...	50	50	50	50
Sensitivity ...	1/5	1/5	1/10	1/10

Fig. 1—Polarograms for Butter Yellow at pH 9.15 showing Three-tangent Construction for measuring Wave Height. The upper waves are due to the  $\text{azo}$  group, the lower to the pilot ion  $\text{Ti}^{+}$ .



only the dye concentration being changed from one to another. This avoided variations in pH and in ionic strength. With the same concentrations of base and buffer electrolytes, change from water to aqueous alcohol as the medium caused a change of pH from 4.75 to 4.65 for the acid solution and from 9.25 to 9.15 for the alkaline.

In general, it was found that an alkaline buffer was to be preferred, since this led to greater solubility of the acid dyes, which were in the majority in the selection taken. It was also noted that gelatin and ethyl alcohol present together in a solution each tended to impair the peak-suppressing efficiency of the other.

The procedures for purifying each of the dyes call for no special comment, and they are indicated in Table I. As a criterion of purity, either the constancy of the optical density in standard solution after repeated crystallisation was accepted, or, with dyes in which this was difficult to attain, or where the extent of hydration was doubtful, volumetric determinations by the titanous chloride method were carried out. When commercial products were used as the starting material in the preparation, they came, as indicated, from Imperial Chemical Industries Ltd., Dyestuffs Division (ICI); Indústria Nacional de Produtos Químicos—Geigy (INAC); Société Anonyme de Matières Colorantes et Produits Chimiques Francolor (Fran). Where possible the English version of the commercial name is given.

#### Experimental Results

The essential data are summarised in Table I and Fig. 2.

#### DISCUSSION

##### Qualitative Analysis

There are a number of ways in which the characteristic shape of a polarogram might contribute to the identification of the dye which gives rise to it. One of these may be perfectly general in application, that is the value of the half-wave potential due to the azo group, if that value can be shown to be independent of concentration. Since there is at least one azo group in all the compounds it is proposed to discuss, an attempt has been made to adjust the conditions of working, as already explained, so that a well defined wave, attributable without any ambiguity to this group, is formed. In all cases, when the measurement was made in a well buffered solution with the tendency to form a maximum suppressed, the half-wave potential has been found to be substantially independent of dye concentration. Since this value is a measure of the ease of reduction of the azo group, it is expected that it will be modified by the number, kind, and position of other strongly electropositive or electronegative groups within the molecule. As a further means of identifying individual dyes, the formation of waves ascribable to groups other than azo may be of assistance.

From the results of the present survey, in which the variety of conditions in which examination has been made is admittedly rather restricted, the prospect of constructing a complete scheme for

identification is not encouraging. Following are some comparisons that can be made, using the data of Table I—

(i) With a buffer giving pH 4.75, the difference between extreme values of  $E_1$  for -N=N- is 0.2 v.: Methyl Red -0.22 v., Amidonaphthol Red G -0.42 v.

(ii) With a buffer giving pH 9.15-9.25, the greatest difference for  $E_1$  does not occur with the same dyes as in (i) above. It is 0.29 v.: Azo Yellow FFN -0.48 v., Diamine Sky Blue A -0.77 v.

(iii) Among the acid dyes only, the greatest values for  $\Delta E_1$  are 0.19 v. with the acid buffer (Methyl Orange and Amidonaphthol Red G), and 0.18 v. with the alkaline buffer (Azo Yellow FFN and Naphthalene Scarlet 4R).

(iv) Among the direct cotton dyes, the greatest values for  $\Delta E_1$  are 0.13 v. with the acid buffer and 0.15 v. with the alkaline (both for Benzopurpurin 10B and Diamine Sky Blue A).

Compared with any single value for  $E_1$  these values for  $\Delta E_1$  seem to be reasonably large, but it is to be remembered that they are for extreme values only, and within this range there are many values that differ from each other by amounts of the same order as that of the experimental error. There seems to be no simple relationship between the constitution of the dye and the value for  $E_1$ . This is shown in Table II.

TABLE II  
Difference of Half-wave Potentials for Pairs of Chemically Related Dyes  
(pH = 9.15-9.25)

Dyes	Chemical Difference	$\Delta E_1$ (I - II)
Butter Yellow (I) Methyl Orange (II)	II = I + SO <sub>3</sub> Na	-0.05
Metanil Yellow (I) Orange IV (II)	I m-SO <sub>3</sub> Na II p-SO <sub>3</sub> Na	-0.03
Azo Yellow FFN (I) Orange IV (II)	II = I + (NO <sub>2</sub> ) <sub>2</sub>	+0.07 (for N:N)
Butter Yellow (I) Methyl Red (II)	II = I + COONa	-0.14
Congo Red (I) Benzopurpurin 10B (II)	II = I + (O-CH <sub>2</sub> ) <sub>2</sub>	-0.06
Chlorazol Sky Blue FF (I)	I 5:7:5':7' (SO <sub>3</sub> Na) <sub>4</sub>	+0.13
Diamine Blue A (II)	II 3:6:3':6' (SO <sub>3</sub> Na) <sub>4</sub>	

The comparison in Table II suggests that the most that could be hoped for would be the possibility of distinguishing between certain isomeric dyes, and perhaps of showing their proportions in admixture. In any continuation of this work, there are a number of expedients that are commonly used by polarographers which might be successful in causing a greater distinction between the values for  $E_1$  of selected dyes. For instance, a wider variety of solvents could be tried, and, in a mixture of two dyes with their values for  $E_1$  close together, two polarograms could be made, one in a solvent which would change the value of  $E_1$  most for the first dye, the second in a solvent which would change the value most for the remaining dye. Since many dyes can form complexes with metallic

ions, these can be used, in the inverse sense to the way in which they are commonly used in the polarography of inorganic compounds, viz. to suppress or displace the characteristic wave of one dye in a mixture. There is an example in the present series when Eriochrome Brown R is polarographed in the presence of nickel, and the nickel wave is suppressed completely while the waves for both the azo and the nitro groups are rendered more negative. Thus, when a mixture of Eriochrome Brown R and Chrysoidine R is polarographed in the absence of nickel in an alkaline medium, the respective waves for the azo group overlap. If nickel is added, it combines with the Eriochrome Brown R only, displacing the wave for the azo group, so that the corresponding waves for the two dyes are now fully separated.

#### Quantitative Determinations

In the experimental section it was seen that there was a linear relation between wave height and concentration of dye for most of the dyes examined, over a useful range of concentration. This forms a pragmatic justification for the use of this method with the selection of dyes examined here, but these, although widely representative, are only a small number compared with the total number of water-soluble dyes which might be eligible for similar estimations. Some of these may be unusual or distinctive in their polarographic behaviour, so that it is desirable, even at this preliminary stage, to consider the principles of the method a little more critically.

The fundamental relation between wave height and concentration  $C$  is expressed in the equation of Ilkovič—

$$i_d = KnCD^{1/2}m^{1/2}t^{1/2} \quad (i)$$

( $i_d$  = mean electrolysis current during the life of a mercury drop;  $n$  = number of Faradays per mole of dye reduced;  $D$  = diffusion coefficient of the diffusing particles (molecules or aggregates) of the dye;  $m$  = weight of mercury passing the jet (mg./sec.);  $t$  = time (sec.) for the formation and detachment of a single drop;  $K$  is a constant). It will be seen that, when drop formation is regular, there will be a linear relation between  $i_d$  and  $C$ , and hence between  $h$  and  $C$ , providing that  $D$  does not change. So far, it has been assumed that the diffusion coefficient of the dye will remain independent of concentration if it is certain that the diffusing units remain constant in size and charge. This is attained most simply by keeping the dye molecularly dispersed over the concentration range in which the measurements are to be made. This may mean the use of solvents other than water for dyes that show signs of aggregation as the concentration is increased. The change in the polarographic characteristics of a dye after complex formation with a metal is due in part to a change in the diffusion coefficient of the diffusing particles.

The reliability of the method can be assessed by the fit of the experimental points to the linear curves passing through the origin in Fig. 2. With most of the dyes it has been possible to produce at least one calibration curve in which the error does

not exceed  $\pm 1.5\%$ . This compares favourably with the value of  $\pm 1\%$ , which is the best accuracy claimed for the estimation of dyes with simple photoelectric absorptimeters. Once a calibration curve has been constructed for a dye, an actual estimation should not take longer than 30 min. for a pen-recording instrument, a little longer if the trace is photographic and requires development.

Where a suitable metal ion, with a value for  $E_1$  similar to that of the dye, can be introduced, the pilot-ion procedure is advantageous, since it eliminates those sources of error, e.g. change in temperature, irregularities in the performance of the capillary, etc., which have approximately the same effect on the metal ion and the dye molecule. Gilbert and Rideal have shown that it is possible to estimate a soluble azo dye in solution when the volume of solution available is so small that normal colorimetric estimation becomes inconvenient. They have also discussed the interference that sometimes occurred in the micro-cells they used (with mercury pool anode) because the concentration of dye could change appreciably during a determination, and because oxidation products from the anode region could diffuse back into the cathode region.

#### Number of Electrons transferred during Cathodic Reduction

It has already been seen that each azo group appears to be capable of reduction to different stages in a polarographic determination, taking up two electrons for transformation presumably to the hydrazo stage as recorded by Shikata and Tachi<sup>10</sup> or four for complete scission as noted by Gilbert and Rideal<sup>11</sup>. For a symmetrical disazo dye, four or eight electrons will be necessary for each molecule, according to the stage to which the reduction is carried. The numbers two or six are less likely, because (a) it is not probable that only one azo group will be reduced and the other left intact or (b) it is not very probable that the respective azo groups will be reduced in different ways within a symmetrical molecule. For an asymmetrical disazo dye, in which the reduction potentials of the individual azo groups could differ appreciably, the number six is more likely.

It appears possible to deduce the number of electrons required for a few dyes by one or other of two methods—

(i) Application of the Ilkovič equation.

(ii) Comparison of the heights of the different waves in the polarogram of a dye which has reducible groups in addition to the azo groups.

(i) If the Ilkovič equation in its normal form (i) is taken to define the wave for the dye, and the polarogram is taken in the presence of a metal pilot ion, the wave for the latter will be defined by—

$$i_d = Kn'C'D^{1/2}m^{1/2}t^{1/2} \quad (ii)$$

$K$ ,  $m$ , and  $t$  are instrumental constants and are therefore common to both equations. Dividing (i) by (ii)—

$$\frac{i_d}{i_d'} = \frac{nCD^{1/2}}{n'C'D^{1/2}} \quad (iii)$$



If  $h$  and  $h'$  are the respective wave heights of the dye and the pilot ions,  $h = ki_d$  and  $h' = ki_d'$ , where  $k$  is a constant of the galvanometer and depends only on the sensitivity. Substituting in (iii)—

$$\frac{h}{h'} = \frac{nCD\frac{1}{2}}{n'C'D'\frac{1}{2}} \quad (\text{iv})$$

From (iv) the value for  $n$  can be calculated if all the other quantities are known. As already indicated, this approach is a convenient one, since the comparison of the waves of dye and pilot ion eliminates the need for taking into account the effect of temperature upon the diffusion coefficient, irregularities in the behaviour of the capillary, and the actual value of  $K$  itself.

Diffusion coefficients for some of the dyes examined, measured at room temperatures and at concentrations within the range of those employed here, have been given by E. Valkó<sup>14</sup>. Substituting these, the following values for  $n$  were obtained—

Metanil Yellow	...	...	1.7
Methyl Orange	...	...	1.8
Orange II	...	...	4.0
Naphthalene Scarlet 4R	...	...	3.9
Congo Red	...	...	4.3
Chlorazol Sky Blue FF	...	...	6.4

For the first four dyes, all monoazo, the calculation gives a clear indication of the corresponding integral value of  $n$ , and shows that sometimes two and sometimes four electrons per azo group can be added. Congo Red has a symmetrical molecule, and the result suggests that two electrons are used in reducing each of the two azo groups. The result for Chlorazol Sky Blue FF is ambiguous. This may be a reflection of the difficulty of determining accurately the diffusion coefficient of this dye.

(ii) When a dye has two groups which are reduced at different potentials, two waves are obtained, and the height of each wave is proportional to the number of electrons required to reduce the corresponding group. With Azo Yellow FFN and Eriochrome Brown R, both azo and nitro groups are present. For Azo Yellow FFN, the heights of the two waves are equal. Since the number of electrons required to reduce a nitro group may be 2, 4, or 6, the two nitro groups in this dye will require 4, 8, or 12 electrons. Four is the only possible number common to the one azo and two nitro groups, and it is concluded that this number of electrons is used in the reduction of the azo group. In Eriochrome Brown R, the ratio—

$$\frac{h_{\text{azo}}}{h_{\text{nitro}}} = \frac{1}{2}$$

Here there are one azo and one nitro group present in the molecule. To the possible values of 2 or 4

for the azo group there will correspond the values of 3 or 6 for the nitro group. Since, for the latter, only the value 6 is permissible, it is concluded that four electrons are required for the azo group.

\* \* \*

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## The Rotproofing of Viscose Rayon

### II—Treatment of Viscose Rayon with Iron and Chromium Salts

J. W. BELL and MARGARET M. RAMSEY

Although Mineral Khaki\* treatments are recommended for proofing cotton against micro-organisms, certain types of chromium and iron pigmentation are shown to be relatively ineffective when applied to viscose rayon, at least when fairly drastic test methods are employed. This is in agreement with results previously obtained with cotton<sup>1,2</sup>. The proof is slightly improved by using potassium chromate as the developing agent, but the sexavalent chromium produced is not fast to leaching. Little improvement is effected by incorporating copper. The viscose rayon takes up considerably less pigment than does cotton under similar conditions, but even where the amounts are almost the same the rayon is still much less resistant to micro-organisms. This difference may be partly due to the lower inherent resistance of viscose rayon. When chromate development is used the rayon appears to be less damaged (as measured by caprammonium fluidity) than cotton similarly treated.

Mineral Khaki\* has been used for many years as a cheap pigment for cotton materials, and more recently attention has been paid to its rotproofing effects. It is generally accepted that the iron functions as a pigment only, but the use of iron and chromium, or chromium alone, is officially recommended for the purpose of rotproofing<sup>3</sup>. The process has been employed in many investigations by other workers, e.g. Neill and Travers<sup>4</sup> and Weatherburn and Bailey<sup>1,2</sup>, while studies of the mechanism have been made by Fargher<sup>5</sup> and by Race *et al.*<sup>6-14</sup>. There is, however, little information on the use of such pigments on viscose rayon. The following account describes work carried out to study the effect of certain treatments, similar to the application of Mineral Khaki, on the resistance of viscose rayon to micro-organisms.

#### PREPARATION OF MATERIALS

Continuous-filament viscose rayon yarn (standard S twist, 500-denier, 50-filament, supplied by Messrs. Courtaulds Ltd.) was used throughout, and was wound into hanks and purified as described in Part I<sup>15</sup>.

#### APPLICATION OF MINERAL KHAKI AND ITS FASTNESS TO LEACHING

Mineral Khaki is applied to cotton by impregnation of the material in a bath containing chromium and either ferric or ferrous iron, followed by development in a second bath with alkali or, for the purpose of producing sexavalent chromium, with potassium chromate. By employing different alkali developers it is possible to vary the amounts of chromium and iron deposited. According to Race *et al.*<sup>7</sup> the method of development has some influence on the subsequent resistance to micro-organisms; development in an ammoniacal solution appeared to give the best results.

Initially five methods of development were studied. Hanks of viscose rayon, each weighing approx. 2 g., were conditioned at 65% R.H. and 22-2°C. for at least a week, and their weights determined accurately. Batches of 22 hanks (in the case of chromate development, 44) were wetted out

overnight in distilled water, and "dyed" and developed as summarised in Table 1. In all cases treatment was for 15 min. with a bath containing, per litre, 150 g. of chrome alum and 50 g. of either iron alum (for Fe<sup>3+</sup>) or ammonium ferrous sulphate (for Fe<sup>2+</sup>). In Method 2 treatment was at room temperature; in all other cases at 90°C. Development was in all cases for 15 min.

TABLE I  
Methods of Development

Method	Bath	Concn. (g./litre)	Temp. (°C.)
1	NaOH	34	80
	Na <sub>2</sub> CO <sub>3</sub>	100	
2	Na <sub>2</sub> CO <sub>3</sub>	2.75	50
3	Ammonia	55*	80
	(sp.gr. 0.880)		
4	Ammonia	44*	Room temp.
	(sp.gr. 0.880)		
	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	40	
5	K <sub>2</sub> CrO <sub>4</sub>	50	80

\* ml./litre

In each case a liquor:yarn ratio of 20:1 was used. The yarn in the baths was stirred at regular intervals and, between impregnation and development, was squeezed through rollers, the pressure being constant throughout the experiments. After development the hanks were washed rapidly in distilled water, which was followed by prolonged washing in running tap-water. Examination of filament cross-sections showed that penetration of the pigment was even and complete. Hanks were removed for analysis at intervals up to 264 hr., and total chromium, total iron, and sexavalent chromium were determined according to the method described by Race *et al.*<sup>8</sup>. Results were calculated on the dry weight of the untreated hanks. The initial chromium and iron contents (i.e. after 3 min. washing) are shown in Table II; as over 200 determinations were carried out, the detailed results are not presented. There appears to be very little difference in the fastness to leaching of the pigments developed by the five different methods; prolonged washing in tap-water produces in general very little loss of iron or chromium. Exceptions are—yarn dyed in ammonium ferrous sulphate and chrome alum, and

\* This name is used here for the sake of convenience; it is not suggested that the treatments described, resulting in the formation of mixtures of chromium and iron oxides, are identical with any particular commercial method of dyeing Mineral Khaki.

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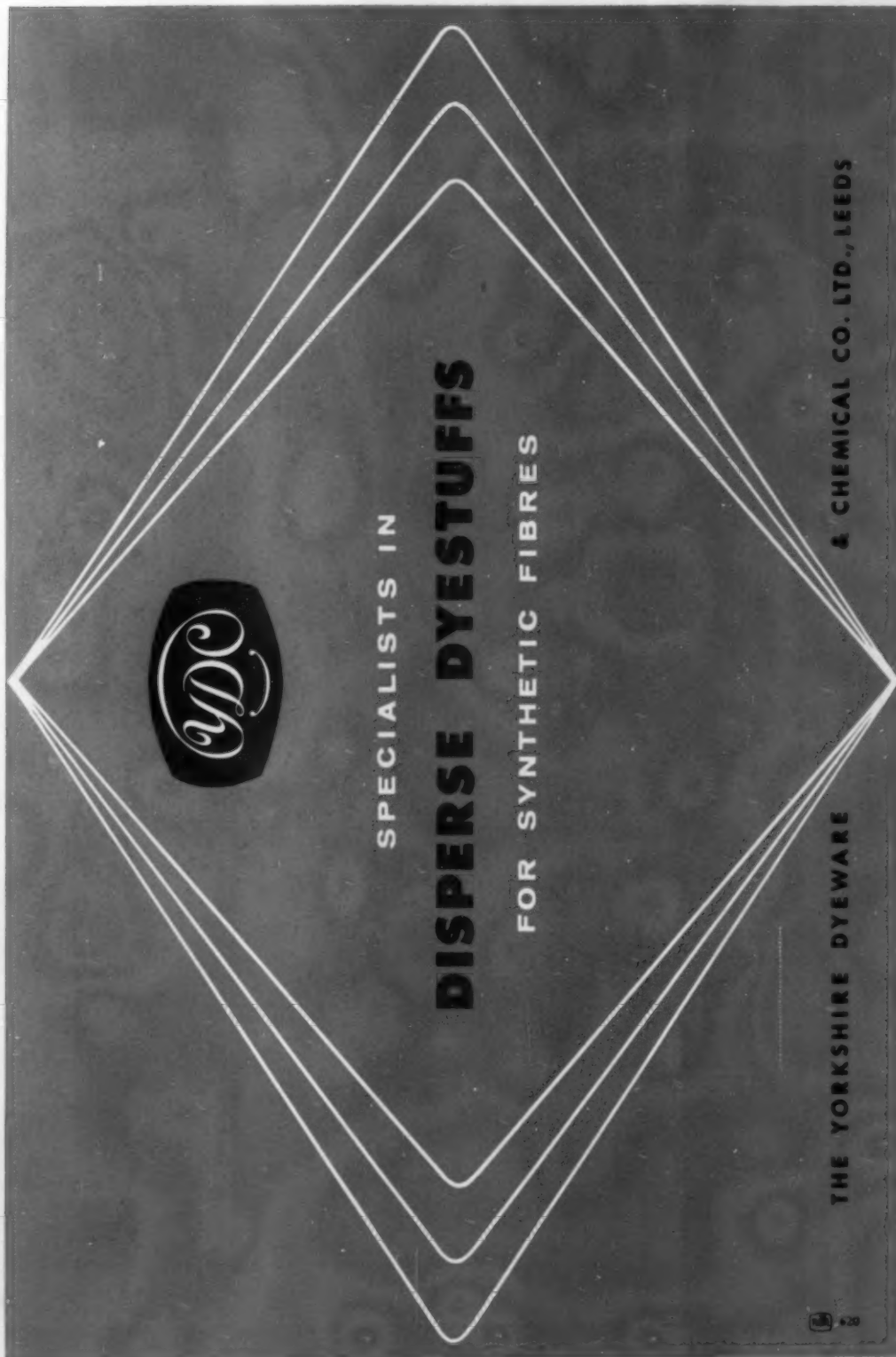
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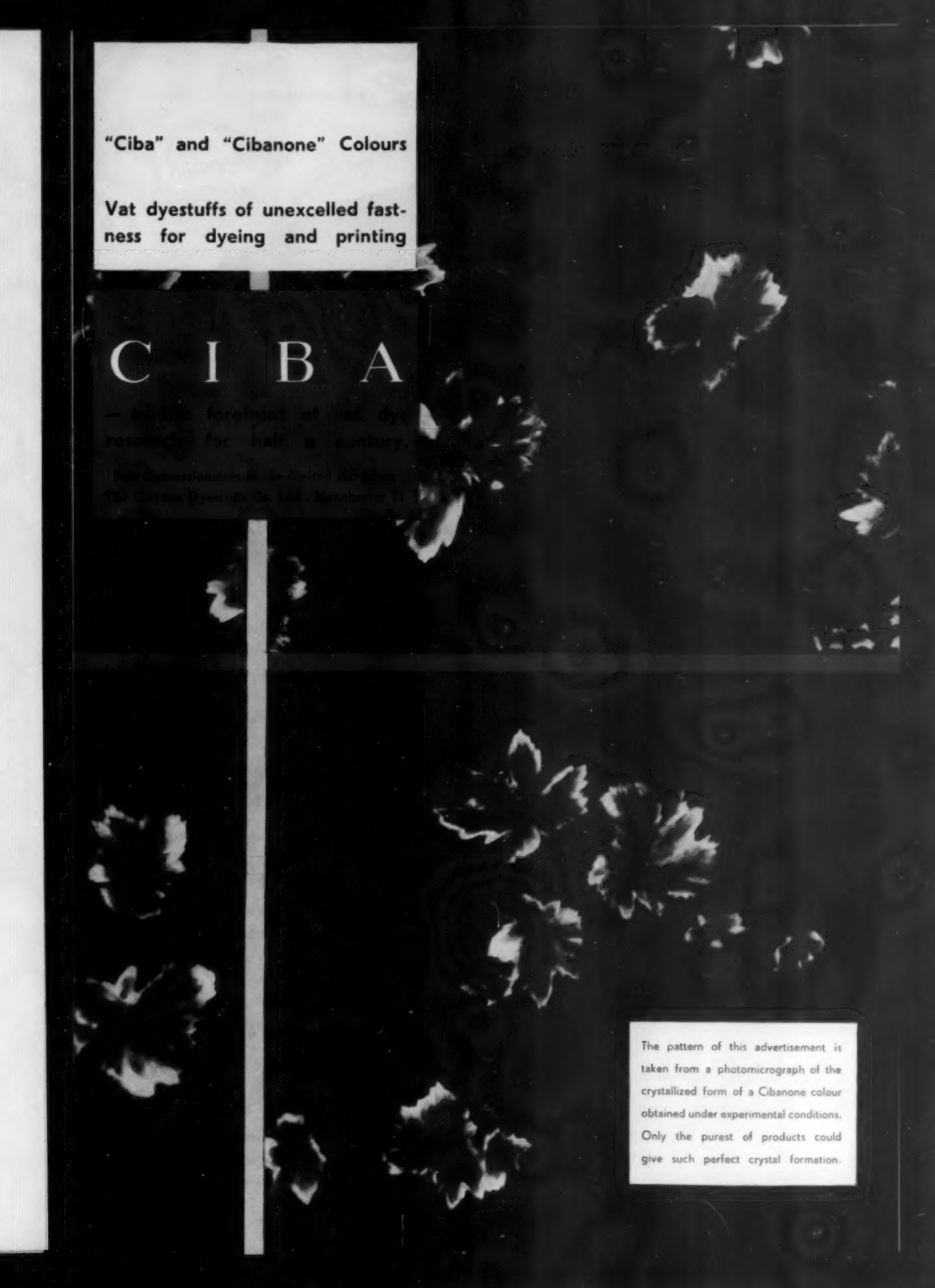
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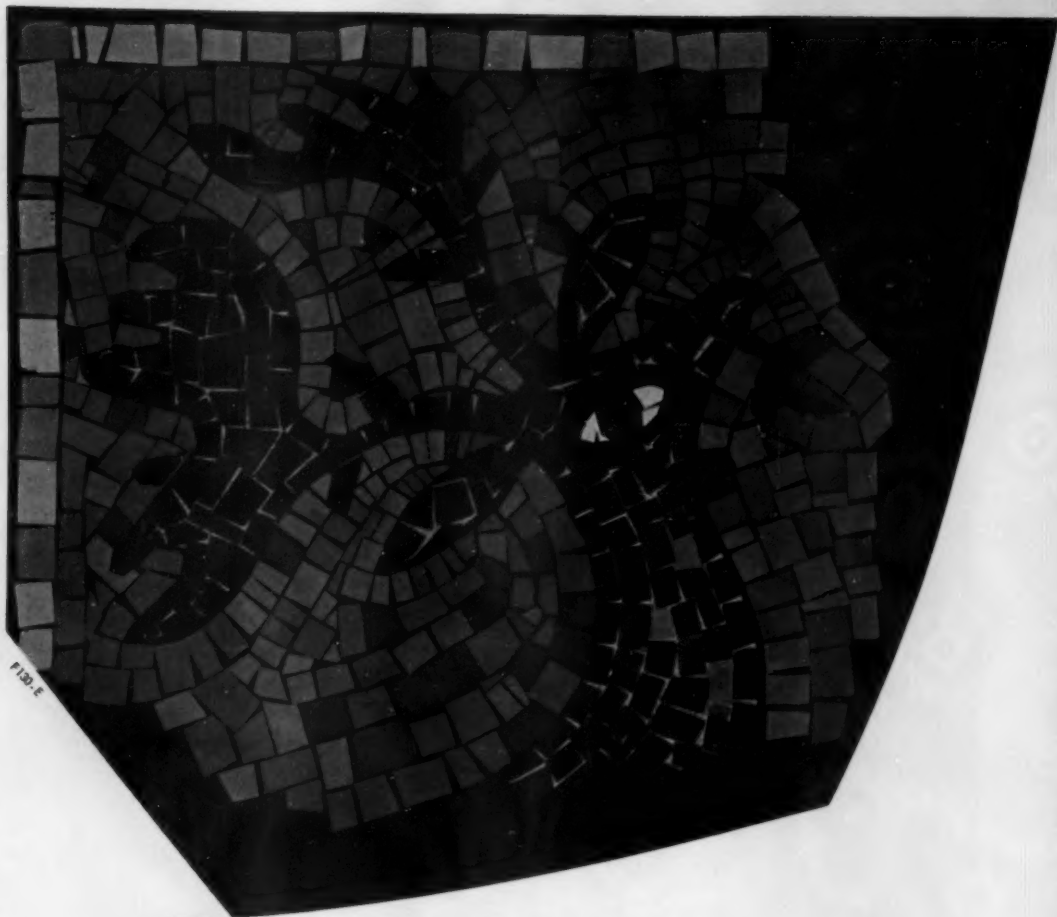
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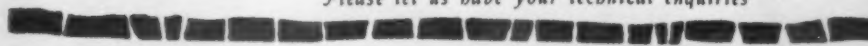
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developed in sodium carbonate, which loses about 25% of the chromium present; and chromate-developed yarn, in which the iron is fast and the hexavalent chromium is almost entirely lost after 4 hr. (with  $\text{Fe}^{3+}$ ) and after 1 hr. (with  $\text{Fe}^{2+}$ ).

TABLE II

**Analysis of Viscose Rayon Yarn dyed with Mineral Khaki and developed by Different Methods**

Method	State of Metal to Bath	Metal in Yarn (%) Total Fe (as $\text{Fe}_2\text{O}_3$ )	Total Cr (as $\text{Cr}_2\text{O}_3$ )	$\text{Cr}^{VI}$ (as $\text{Cr}_2\text{O}_3$ )	Wash Total Oxides
1	$\text{Fe}^{2+}$	0.80	1.49	—	2.29
	$\text{Fe}^{3+}$	0.81*	1.94*	—	2.75*
2	$\text{Fe}^{2+}$	0.10	0.23	—	0.33
	$\text{Fe}^{3+}$	0.46	0.52	—	0.98
3	$\text{Fe}^{2+}$	0.81	1.37	—	2.18
	$\text{Fe}^{3+}$	0.63	1.23	—	1.86
4	$\text{Fe}^{2+}$	0.68	1.20	—	1.88
	$\text{Fe}^{3+}$	0.54	0.95	—	1.49
5	$\text{Fe}^{2+}$	0.65	1.86	0.58	2.51
	$\text{Fe}^{3+}$	0.61	1.30	0.41	1.91

\* After 30 min. rinse

**RESISTANCE OF TREATED SAMPLES TO MICRO-ORGANISMS**

*Test Methods*

The dyed yarn was tested by exposure to a pure culture of *Chaetomium globosum*, to a solid horse-dung preparation, and to a horse-dung liquid extract. After incubating for different times the strength of the yarn was measured on a Baer single-thread strength tester, using wet yarn and a short test length. Full details of all the techniques have been given in Part I<sup>18</sup>.

*The Effect of using Different Developers*

Preliminary experiments were carried out to ascertain whether yarns containing approximately the same amounts of chromium and iron, but developed by different methods, were equally susceptible to attack by micro-organisms. Hanks were dyed and developed by the five methods described above, deposits of approx. 1.4% chromium (as  $\text{Cr}_2\text{O}_3$ ) and 0.9% iron (as  $\text{Fe}_2\text{O}_3$ ) being produced by adjusting the strengths of the dyebaths. The samples were washed in running water for 24 hr. and dried in air. Short rotproofing tests were carried out, using *C. globosum* and horse-dung liquid extract, breaking strengths being assessed after one and three weeks. Apart from the somewhat greater efficiency of the chromate development, there was no significant difference in the proofing efficiency of the pigments produced by the five methods; in all instances the proof was only feeble. It was decided, therefore, in the further experiments to vary the amount of oxides deposited by using the different development methods. Deposits of chromium of from 0.3% to 1.4% were obtained (1% Cr is sufficient to satisfy specification requirements<sup>3</sup>), and after development the yarn was centrifuged for 5 min. instead of being squeezed through rollers. It was washed for 24 hr. in running water before drying, except in

the case of chromate-developed yarn, which was washed for only 1 hr. to ensure the retention of some hexavalent chromium.

A total of ten treatments were applied, comprising four different concentrations of trivalent chromium, each with  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in the bath, and two different concentrations of hexavalent chromium, one with  $\text{Fe}^{2+}$  and one with  $\text{Fe}^{3+}$  in the bath. Yarns so treated were each tested by the three incubation methods, and strength measurements were carried out, in general, after 4, 7, 14, 21, 28, 42, and 63 days. For the sake of brevity these (approx. 230, including the control) results cannot be presented in detail, but the values recorded after 28 days are summarised in Table III. All results are expressed as percentages of those obtained with yarn which has been treated. Loss in strength due to the treatment is discussed separately.

Taken as a whole, the results show clearly that this type of Mineral Khaki is relatively ineffective as a proofing agent for viscose rayon where severe test conditions are employed. Degradation by *C. globosum* is to some extent retarded, but when the horse-dung contact test is used the degradation is in all instances accelerated by the presence of the pigment. The concentrations of chromium and iron present do not seem to have much influence on the result. Hexavalent chromium gives markedly improved results: in some cases as much as 50% strength was still retained after nine weeks in *C. globosum*, but the horse-dung tests were less promising. It is probable that the presence of reducing matter serves to bring the proof to the same condition as when trivalent chromium is used. This was confirmed by analysis, which indicated that hexavalent chromium was most rapidly eliminated in the contact test and least rapidly when a pure culture was employed. It is of interest to record that particularly variable results were obtained between duplicate determinations, in marked contrast to the earlier leaching experiments, in which excellent reproducibility was obtained.

*Incorporation of Copper with the Mineral Khaki*

An attempt was made to improve the resistance of the treated yarn by incorporating copper, a method previously used by e.g. Race *et al.*<sup>12</sup> and Weatherburn and Bailey<sup>2</sup>. A batch of viscose rayon hanks was wetted out overnight in distilled water and treated in a bath containing, per litre, 150 g. of chrome alum, 50 g. of iron alum, and 25 g. of hydrated copper sulphate, at room temperature for 15 min. The hanks were then centrifuged for 3 min., and developed in a 0.275% solution of anhydrous sodium carbonate for 15 min. at 50°C. A liquor : yarn ratio of 20 : 1 was employed. They were finally washed in running tap-water for 24 hr. and dried in air. Analyses of chromium, copper, and iron were carried out according to the procedure used by Race *et al.*<sup>12</sup>; values recorded were 0.45% chromium (as  $\text{Cr}_2\text{O}_3$ ), 0.44% copper (as Cu), and 0.44% iron (as  $\text{Fe}_2\text{O}_3$ ).

Samples of yarn treated by the above method were tested by the three incubation procedures.

TABLE III

Residual Strength, after 28 days' Incubation, of Yarn treated in Different Ways and tested by Three Methods

Total Cr as $\text{Cr}_2\text{O}_3$ (%)	State of Fe in Bath	Fe as $\text{Fe}_2\text{O}_3$ (%)	Cr VI as $\text{Cr}_2\text{O}_3$ (%)	<i>C. globosum</i> Test	Strength (%)	
					Contact Test	Horse-dung Extract Test
Control	—	—	—	11	20	11
0.5	$\text{Fe}^{2+}$	0.45	—	23	9	60
0.8	$\text{Fe}^{2+}$	0.50	—	20	9	6
1.1	$\text{Fe}^{2+}$	0.60	—	23	16	35
1.5	$\text{Fe}^{2+}$	0.75	—	21	12	12
0.3	$\text{Fe}^{2+}$	0.10	—	13	14	13
0.9	$\text{Fe}^{2+}$	0.45	—	16	3	12
1.1	$\text{Fe}^{2+}$	0.60	—	30	17	37
1.5	$\text{Fe}^{2+}$	0.80	—	24	8	3
1.31	$\text{Fe}^{2+}$	0.60	0.41	63	22	65
1.67	$\text{Fe}^{2+}$	0.65	0.46	75	—	51

In general, it was found that an improvement had been brought about in the pure culture and horse-dung contact tests, but that in horse-dung liquid extract the proof was less effective than with Mineral Khaki alone. Values after 28 days' incubation are shown in Table IV.

TABLE IV

Residual Strength of Yarns treated with Mineral Khaki and Copper and incubated for 28 days by Three Methods

Method of Test	Control	Residual Strength (%)	
		0.5% $\text{Cr}_2\text{O}_3$ No Cu	0.45% $\text{Cr}_2\text{O}_3$ 0.44% Cu
<i>C. globosum</i> pure culture ...	11	22	40
Horse-dung contact	20	9	29
Horse-dung extract	11	60	8

The severe loss of strength when tested by the horse-dung extract method may be due to loss by leaching, as analysis showed that 62% of the copper had been removed after 28 days, compared with 22% in the contact test and 23% in the pure culture.

#### Comparison with Cotton treated with Mineral Khaki

The results obtained above show that Mineral Khaki on viscose rayon affords a proof greatly

inferior to that which, according to the literature, it gives when applied to cotton<sup>12</sup>. Experiments were therefore carried out to provide a measure of direct comparison. Hanks of cotton yarn, each weighing approx. 2 g., were impregnated and developed to Mineral Khaki by the five methods described earlier, the solution concentrations all being such that about 1.4% of  $\text{Cr}_2\text{O}_3$  would be deposited on viscose rayon. Treated samples were incubated by the *C. globosum* pure culture method and strength tests were carried out after 7 and 21 days. Results obtained are given in Table V, together with results previously obtained in preliminary experiments with viscose rayon. Values for iron content are omitted, as they were very similar both for cotton and for viscose rayon, being about 1.1 and 0.9% respectively.

It is at once evident from Table V that, when treated under identical conditions, cotton is "dyed" considerably more deeply than viscose rayon; secondly, even where the quantities of pigment are almost the same the treated viscose rayon is much less resistant to micro-organisms than is the cotton. Examination of the control values suggests that this may to a large extent be due to the much lower inherent resistance of viscose rayon.

TABLE V

Comparison of Mineral Khaki on Cotton and on Viscose Rayon

Treatment	Developer	$\text{Cr}_2\text{O}_3$ (%)		Residual Strength (%)			
		Cotton	Viscose Rayon	7 days	21 days	7 days	21 days
Control, no proof		—	—	74	56	43	9
Chrome alum and iron alum	$\text{Na}_2\text{CO}_3$	1.2	1.27	93	70	39	29
	$\text{NH}_4\text{OH} + (\text{NH}_4)_2\text{CO}_3$	1.7	1.47	86	59	46	32
	$\text{NaOH} + \text{Na}_2\text{CO}_3$	2.1	1.23	105	71	41	28
	$\text{NH}_4\text{OH}$	3.1	1.47	90	77	48	31
	$\text{K}_2\text{CrO}_4$	—	1.41	94	66	51	41
Chrome alum and ferrous ammonium sulphate	$\text{Na}_2\text{CO}_3$	1.7	1.40	82	58	43	25
	$\text{NH}_4\text{OH} + (\text{NH}_4)_2\text{CO}_3$	1.3	1.35	81	77	50	30
	$\text{NaOH} + \text{Na}_2\text{CO}_3$	2.3	1.50	94	80	46	31
	$\text{NH}_4\text{OH}$	2.6	1.46	82	56	43	28
	$\text{K}_2\text{CrO}_4$	3.0	1.43	104	104	56	41



TABLE VI

## Effect of Mineral Khaki Treatment on the Strength of Viscose Rayon

Developer	Reduction in Strength (%)		Cuprammonium Fluidity	
	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Fe <sup>2+</sup>
Control, no "dye" ...	0	0	8.8	8.8
Na <sub>2</sub> CO <sub>3</sub> ...	13	11	9.6	9.6
NaOH + Na <sub>2</sub> CO <sub>3</sub> ...	24	26	10.0	12.4
NH <sub>4</sub> OH ...	16	13	10.9	12.3
NH <sub>4</sub> OH + (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> ...	29	27	11.5	12.6
K <sub>2</sub> CrO <sub>4</sub> ...	30	37	12.1	13.3

## EFFECT OF MINERAL KHAKI "DYEING" ON THE STRENGTH OF VISCOSE RAYON

It was shown by cuprammonium fluidity and strength measurements that the viscose rayon lost up to about 30% (37% for hexavalent chromium) of its wet tensile strength as a result of the Mineral Khaki treatment. The yarns were rinsed in running water for 24 hr. after the treatment (1 hr. in the case of hexavalent chromium).

The cuprammonium fluidities were measured by the method of Launer and Wilson<sup>18</sup>, the pigment first being removed by shaking 2-g. hanks for 14 hr. with 50 ml. of 0.1 N. ammonium ferrous sulphate solution. Results are shown in Table VI.

It is clear that the treatment itself causes quite a serious loss in strength. The fluidity values are, however, considerably lower than those determined by Race *et al.*<sup>6</sup> for cotton dyed with Mineral Khaki, where fluidities of about 25 were recorded for yarn developed in potassium chromate, rinsed for 1 hr., and dried. It appears that the cellulose chains in viscose rayon, being already much shorter than those in cotton, are not further degraded to a comparable extent.

\* \* \*

The authors wish to record their appreciation of advice and assistance from Professor C. S.

Whewell. One of us (M.M.R.) is indebted to the British Rayon Research Association for the grant of a scholarship.

DEPARTMENT OF TEXTILE INDUSTRIES  
THE UNIVERSITY  
LEEDS 2

(Received 15th September 1955)

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## Notes

## Deaths

It is with great regret that we have to report the loss by death of Mr. H. Jennison (Honorary Treasurer of the Society) and Mr. L. Mills.

Meetings of Council and Committees  
March

Council—7th  
Finance and General Purposes—7th  
Publications—20th  
Colour Index Editorial Panel—15th  
Terms and Definitions—8th  
Examinations Board—19th

The Worshipful Company of  
Dyers Research Medal 1954-1955

On the recommendation of the Council of the Society, the Worshipful Company of Dyers has awarded its Research Medal for 1954-1955 to Dr. C. H. Giles as senior author of the papers *A Study of Certain Natural Dyes. I—The Adsorption of Brazilwood and Logwood Colouring Matters by Fibres*, by F. M. Arshid, J. N. Desai, D. J. Duff, C. H. Giles, S. K. Jain, and I. R. Macneal, and *II—The Structure of the Metallic Lakes of the Brazilwood and Logwood Colouring Matters* by F. M. Arshid, R. F. Connelly, J. N. Desai, R. G. Fulton, C. H. Giles, and J. C. Kefalas (*J.S.D.C.*, **70**, 392-411 (Sept. 1954)).

### London Section Essay Competition

To mark the centenary of W. H. Perkin's discovery of the first coal-tar dye to be used commercially, the London Section of the Society is offering a prize of twenty-five guineas for the best essay on *The Influence of Perkin's Discovery, and of the Synthetic Dyes which followed it, on any trade of the candidate's choice*. The money has been given anonymously by a member of the Society. Competitors need not be members of the Society, but they must live, work, or study in the area covered by the Society's London Section, which is South of a line joining Great Yarmouth and Gloucester. They must not have reached the age of 26 years on 31st December 1956, the latest date for receipt of the essays. Full details can be obtained from the Honorary Secretary of the London Section, Mr. H. W. Taylor, 10 Milton Avenue, Sutton, Surrey.

### Education of Textile Chemists in Switzerland

An article by E. Brunnschweiler in the November 1955 issue of *Textil-Rundschau* (10, 611-617) bemoans the fact that insufficient provision is made in Switzerland for the academic study of textile chemistry. The Swiss textile industry is second in importance (after engineering but before metals and watches), and textile finishing employs about 10,000 persons. The article reviews the present provisions for textile education and research in Switzerland, and compares them with those in

other Continental countries, the United Kingdom, and the U.S.A.

### Regrouping of German Dyemaking Firms

Control of the Cassella Farbwerke Mainkur has been acquired in equal parts by Farbenfabriken Bayer, Farbwerke Hoechst, and the Badische Anilin- und Soda-Fabrik. This elimination as an independent entity of the fourth largest producer of dyes in the Federal German Republic is the first re-amalgamation that has occurred among the various companies into which the I.G. was split after the 1939-1945 war. C.O.C.

### Society of British Printing Ink Manufacturers

The above Society, formed by amalgamation between the Federation of British Printing Ink Manufacturers and the British Printing Ink Association, has just been formally inaugurated. Its offices are in Burley House, Theobalds Road, London W.C.2. C.O.C.

### Causes of Fabric Breakdown

The report for 1955 of the Manchester Chamber of Commerce Testing House states that the main causes of fabric breakdown in the cases examined were mildew attack, photodegradation, misuse of bleaching agents during laundering, and too high an ironing temperature of materials containing heat-sensitive fibres such as acetate rayon or nylon.

## New Books and Publications

### Methods of Test for Textiles

B.S. Handbook No. 11

Pp. 461. London: British Standards Institution. 2nd edition 1956. Price, 30s. 0d.

This revised edition has been prepared in a similar manner to the first edition (noticed in J.S.D.C., 66, 290 (1950)): i.e. it is based on British standards, the standard test methods of the Society and of the Textile Institute, and test leaflets prepared by the research associations. These tests have been brought up to date, and a subject index has been added. Omissions are textile terms and definitions and the identification of textile materials, while the section on narrow fabrics has been much reduced in scope.

The six sections of the handbook now deal with — atmosphere and conditioning, yarns, fabrics, colour fastness (the Society's tests, published as *Standard Methods for the Assessment of the Colour Fastness of Textiles*), and chemical tests. A new appendix lists subjects under investigation for the preparation of standard test methods, including removal of added matter from textiles, determina-

tion of flammability, residual copper, and resin content, and testing rotproofed textiles.

C.J.W.H.

### The ISCC-NBS Method of Designating Colors and a Dictionary of Color Names

National Bureau of Standards Circular 553. Pp. v + 158. Washington, D.C. 1955. Price, \$2.00.

This book, as the title implies, is divided into two sections, one which deals with the definition of a comprehensive series of functional colour names in terms of the Munsell notation, and a dictionary which lists the equivalents of 7,500 different descriptive colour names in terms of this series. With the aid of the dictionary it is possible to locate rapidly, in a Munsell Atlas, that group of colours within which any of the names listed will lie, and because of its scope it is possible to compare colour terminology in widely different fields, such as fashion, biology, and dyeing.

For anyone concerned with the correlation of colour terminologies it should form an invaluable source of information and reference.

E. ATHERTON

**Guida dei Principali Prodotti Chimici****Volume Primo**

By Cesare Ferri. Pp. xvi + 737. Bologna: Nicola Zanichelli Soc. p. Az. 1955. Price, 6,000 lire.

This first volume gives brief reviews of the main groups of industrial chemical products, both natural and artificial, arranged in alphabetical order, from *abrasivi* to *zincatura* (*prodotti per bagni galvanici* di—). A second volume will deal with methods of manufacture.

The section on colouring matters (28 pp.) includes outlines of systems of classification, with examples, both according to chemical structure and according to dyeing properties. A "bibliography" lists mainly a few books published in the 1920s (earliest 1877, latest 1934), but does mention that a new edition of the *Colour Index* is "imminent".

Other subjects dealt with include textile auxiliary products (21 pp.), detergents (6 pp.), diazotype (6 pp.), inorganic pigments (9 pp.), and man-made fibres (7 pp.), but colour photography occupies as much as 11 pp. C.J.W.H.

**Abstracts from British and Foreign Journals and Patents**

*The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., 68, 23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

**I— PLANT; MACHINERY; BUILDINGS****PATENTS****Package Dyeing Machine**

Mellor Bromley & Co.

BP 744,418

An open-topped tank outside the path of the liquor in the closed circuit is connected to this circuit at the suction side of the pump so that when the machine is used standing static liquid pressure is applied by the liquid in the container on that being circulated. This compensates for energy-losses in the circuit and gives protection against development of excessive pressure in the closed circuit, e.g. if the circulated liquor is overheated the excess pressure is vented to atmosphere. C.O.C.

**Controlling the Cycle of Operations of Washing, Dyeing, Bleaching, etc. Machines**

I. M. Fisher

BP 743,786

An electro-magnetically stepped uniselector has a pair of contact banks which in conjunction with a set of switches control the timing of the successive stages of an operating cycle. Other contact banks of the uniselector are connected through preselector switches and relays to control the operating conditions of each stage. C.O.C.

**Wet Processing of Textile Fabrics**

BrC

BP 743,659

The fabric is carried by a current of the treating liquor down a series of inclined trays, the trays being preferably placed one below the other so as to receive the liquor and fabric from the preceding tray. Thus there is no tension imparted to the fabric and creasing is impossible. C.O.C.

**Squeeze Rollers**

E. Kusters

BP 743,292

One of the rollers is a hard roller and the other is made up of thin discs arranged along a core and pressed together by axial pressure. The discs are formed of nylon or perlon fibres impregnated with rubber latex. In these discs the fibres lie in layers corresponding to their thickness so that the fibres of one layer do not enter into adjacent layers but are irregularly disposed only in the individual layers. Thus when forming the surface of the roller only fibres lying in radial planes are cut and only such fibres appear in the surface of the roller. Consequently penetration of the surface of the roller into the meshes of the fabric during squeezing is unhindered. This results in very efficient squeezing. C.O.C.

**Traverse Guides for Webs**

A. Monforts

BP 743,903

Two pairs of pivotally supported rollers, each pair engaging one edge of the web, are coupled together so that displacement of one pair caused by deviation of the web simultaneously causes positive adjustment of the other pair of rollers in order to return the web to its normal position. C.O.C.

**Fabric-steaming Machine**

T. Bailey

BP 744,661

In a machine in which the cloth together with a wrapper is wound on a perforated roller and then the cloth and wrapper are unwound, the cloth being run out of the machine while the wrapper is run together with another fabric on to a second perforated steaming roller, the torque needed to turn both rollers is applied to them independently of the fabric and wrapper. This reduces the tension on the wrapper and in the fabric being unwound and also reduces the compression applied by the wrapper to the fabric being wound on to the other roller. C.O.C.

**Needle Bars for Tenters**

A. Monforts

BP 743,333

The needle bar is provided with recesses, gaps or the like so that it has a comb-like shape and the profile of the individual teeth of that shape are such that the surface in contact with the material to be dried is as small as possible and the drying medium has free access to both sides of the edge of the material. C.O.C.

**Cooling and Conditioning Machines**

Arthur Henton & Co.

BP 744,749

The cloth is passed up and down between screens at the top of which there are water troughs. Water overflows from the troughs on to the screens. The water is supplied to the ends of the troughs so that a wave travels along each trough. Most or all of the available water supply can be supplied successively to selected numbers of the water troughs. If the machine has a pump of capacity sufficient to maintain an adequate supply of water to all the troughs, by using the available pressure on only some of the troughs, there is provided the more copious supply of water needed to secure wetting of screens which are comparatively resistant to being wetted with water, e.g. aluminium screens. Thus effective wetting of all the screens can be ensured soon after the machine has been put into operation. C.O.C.



### Unfolding a Longitudinally Folded Length of Fabric

N. Cornah (St. Margaret)

BP 742,758

The folded fabric, e.g. tubular fabric which has been slit along one crease, is drawn over a guide way. The nose of the guide way leads the central longitudinal fold of the fabric over to the upper surface of the guide way. As the fabric passes along the guide way two halves, one on each side of the fold, drape over the sides of the guide way and are spread outwards until they are flush and can be treated as a flat single-thickness fabric.

C.O.C.

### Web Tension Control in Printing Machines

James Halley & Sons

BP 744,032

Constant tension is maintained in a web being fed to a printing machine by allowing a tensioning roll to bear upon the web between two positively driven rolls around which the web passes. The tensioning roll moves in accordance with the length of web between the two driven rolls. As it moves it operates an arm which in turn controls the direction of rotation of a control disc for varying the speed of rotation of one of the driven rolls.

C.O.C.

### Screen Printing Machine

E. Walsh and E. Landesman

USP 2,704,510

The screen is pivoted vertically for movement to and from the horizontal (printing) position. The length of the squeegee's printing stroke can be varied as necessary to accommodate work of varying sizes and shapes.

C.O.C.

### Steam Pressing and Ironing of Garments and Fabrics

L. B. Edwards and H. I. Hersh

BP 743,944

New Products developed since November 1954—

Alphabetical List (IV p. 175)

Dyeing in a Molten-metal Dyeing Machine (VIII p. 189)

Modern Flooding Equipment (X p. 192)

Coating Moving Web with Liquids (X p. 195)

## II—WATER AND EFFLUENTS

### Treatment of Wool-scouring Wastes with Colloidal Bentonite

W. Fong and H. P. Lundgren

Text. Research J., 25, 994-1000 (Dec. 1955)

Addition of an aqueous bentonite dispersion to wool-scouring wastes immediately after conventional acid cracking produces a marked improvement in clarification of the waste liquor. The amount of bentonite required (0.1-0.5%) depends on the grease and suint content of the waste. Treatment of a standard waste with acid and bentonite removed up to 96% of the grease and reduced the chemical oxygen demand by 60%, compared with 67% grease removal and 33% reduction with acid alone.

J.C.F.

#### PATENTS

### Treating Boiler Feed Water

Clayton Manufacturing Co.

BP 744,265

The raw water is subjected to cathodic treatment in a two-compartment diaphragm type of electrolytic cell. The water in the cathode compartment becomes alkaline and so the Mg and Ca compounds are precipitated. At the same time corrosion causing materials, e.g. sulphates and chlorides, concentrate in the anode compartment and are discharged from the system.

C.O.C.

### Treatment of Acid Effluents

Chemieprodukte

BP 744,480

The effluent is passed through a bed of ignited magnesite. This has the advantage over using lime in that no special apparatus is necessary nor is any sludge formed.

C.O.C.

## III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

### Condensed Phosphates

Albright &amp; Wilson Ltd.

Lab. Practice, 5, 23-26 (Jan. 1956)

The preparation, structures, properties, and applications of polyphosphates and polymetaphosphates are reviewed,

and methods for the analysis of mixtures containing these substances are outlined. There are 22 references.

A.E.S.

### Micellar Molecular Weights of some Paraffin-chain Salts by Light Scattering

H. V. Tartar and A. L. M. Lelong

J. Physical Chem., 59, 1185-1190 (Dec. 1955)

Micellar molecular weights in aqueous solution of 13 normal paraffin salts are determined by light scattering. Some comparisons are made of the influence of uni- and bi-valent gonions.

W.R.M.

### Intermediate for Flame-resistant Polymers—Reactions of Tetrakis(hydroxymethyl)phosphonium Chloride

W. A. Reeves and J. D. Guthrie

Ind. Eng. Chem., 48, 64-67 (Jan. 1956)

Tetrakis(hydroxymethyl)phosphonium chloride (THPC) is a crystalline compound soluble in water and lower aliphatic alcohols. It reacts with many substances in a similar manner to formaldehyde. Thermosetting, phosphorus-containing polymers are produced by reaction with urea, melamine, and hydroxymethylmelamines. These resins impart flame resistance to cellulosic fibres. Very insoluble resins containing up to 15% P have been prepared. Resins are formed also with phenol and its derivatives, and with ethyleneimine. THPC behaves similarly to polyhydric alcohols, e.g. glycerol, in forming polymers with polybasic carboxylic acids and anhydrides. In general, the THPC resins are very similar to the corresponding formaldehyde and glycerol resins, except that they are flame-resistant.

W.K.R.

#### PATENTS

### N-Alkyl(or Aralkyl)-substituted Alkylene Polyamine Methylene Phosphonic Acid Compounds—Sequestering Agents and Detergents

Dow Chemical Co.

BP 744,633

Compounds of formula—

$$RN(CH_2PO(OM)_2)_n\text{-Alkylene-}$$

$$[N(CH_2PO(OM)_2)_n\text{-Alkylene}]_n\text{-NA}(CH_2PO(OM)_2)_n$$

(R = Alk or aralkyl of <19 C; A = Alk or aralkyl of <19 C or  $CH_2PO(OM)_2$ ; Alkylene =  $CH_2CH_2$ ,  $CH(CH_3)CH_2$ , or  $CH_2CH_2CH_2$ ; n = 0, 1, 2, 3 or 4; M = H, alkali metal, ammonium or alkylammonium, e.g.  $(HO)_2PO-CH_2-N(C_2H_5)_2-CH_2CH_2-N(CH_2PO(OH)_2)_2-CH_2PO(OH)_2$ , are detergents. Their Al, Ba, Cu and Pb salts are more stable than those of the corresponding carboxylic acids and are more soluble or miscible in organic solvents and hydrocarbon oils.

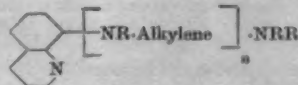
C.O.C.

### Quinoly Aliphatic Alkylene polyamine polyacids

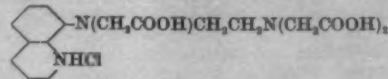
Dow Chemical Co.

BP 744,840

Compounds of formula—



(R =  $CH_2COOM$ ,  $CH_2CH_2COOM$  or the like; M = H, alkali metal, ammonium or subst. ammonium; n = a whole number; Alkylene includes cycloalkylene and interposes 2 or 3 C atoms between the N atoms), e.g.



form very stable chelates with a large number of metals, e.g. Mg, Be and Fe, which are not formed with ethylenediaminetetraacetic acid, somewhat less stable chelates being formed with Ca, La, Fe, Zn and Cd.

C.O.C.

### Poly(hydroxyamino Acid Compounds—Sequestering Agents

Dow Chemical Co.

BP 744,926

Compounds of formula—

$$N(CH_2CH_2OH)_2\text{-CH}_2\text{-CHOH-(CH}_2\text{)}_n\text{-NA-Y-NA-(CH}_2\text{)}_n\text{-CHOH-CH}_2\text{-N(CH}_2\text{CH}_2\text{OH)}_2$$

(Y = bivalent alkylene or cycloalkylene interposing 2 or 3 C atoms between the N atoms attached thereto, such



interposed C atoms carrying H and/or Alk of 1 or 2 C;  $n = 1-4$ ;  $A = CH_3COOH$ ,  $CH_3CH_2COOH$ ,  $CHPO(OH)_2$ ,  $CH_3CH_2PO(OH)_2$  or  $CH_3CH_2SO_3H$ ; e.g.  $NN'$ -di(2-hydroxy-3-iminodithianolpropyl)-ethylenediamine- $NN'$ -diacetic acid, are sequestering agents for metal ions, including iron, in strongly acid to strongly alkaline solution.

C.O.C.

**Sequestering Agents**

Norman Evans &amp; Rais

BP 743,760

An aqueous slurry of ethylenediaminetetraacetic acid is mixed with dilute aqueous sodium silicate. The silicic acid precipitated if dried without being washed, yields a product consisting of the tetrasodium salt of ethylene diaminetetraacetic acid enclosed in a network of silica gel. It dissolves gradually or disintegrates rapidly on contact with water. In the first case an empty structure of silica gel is left after complete leaching out, while in the second case a deposit of coarse silica is left at the bottom of the vessel. The product is very suitable for use in tower softening plants.

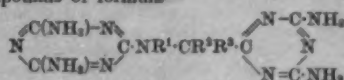
C.O.C.

**Bis-aminotriazine Condensates**

Rohm &amp; Haas Co.

BP 744,674

Compounds of formula—



( $R^1 = \text{Alk of 1-8 C and has a H atom on the C atom next to the N atom}$ ;  $R^2 = \text{H or } CH_3$ ;  $R^3 = \text{Alk of 1-8 C}$ ) react readily with formaldehyde and an alcohol to yield products, some of which are used to render rayon fabrics dimensionally stable, while others reduce the felting power of wool, confer increased wet strength to paper, stiffen nylon, or are dissolved in organic solvents to form coating compositions.

BP 744,675-6

Describes manufacture of compounds of above formula.

C.O.C.

**Methylol Derivatives of Ureido-polyamino-caprolactam Condensates**

Rohm &amp; Haas Co.

BP 744,110

$\epsilon$ -Caprolactam and an alkylene polyamine (alkylene of 2-3 C) are heated in 3:1 to 1:1 mol. proportion at 150-250°C. until a soluble condensate is obtained. This is then heated with urea (1 mol. urea to each 2 imino or amino groups) at 100-200°C. so that ammonia is driven off. The resulting condensate is then heated with formaldehyde at 10-100°C. The products are hydroxymethyl derivatives useful for imparting dimensional stability to cotton, rayon and wool fabrics, for improving the adhesion of rubber to cotton or rayon and for improving the wet strength of paper. Treating them with alcohols yields the alkoxy-methyl derivatives which are usually soluble in polar solvents and are used in coatings to be resistant to non-polar solvents.

C.O.C.

**Rotproofing Compositions for Cellulosic Products**

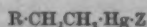
F. W. Berk &amp; Co.

BP 743,154

Compounds of formula—



( $Y = \text{Ar}$ ;  $X = \text{acetate, chloride, nitrate, hydroxide, bromide or iodide}$ ) dissolved in a solution of a compound of formula—



( $R = \text{alkoxy or arylalkoxy}$ ;  $Z = \text{acetate, borate or lactate}$ ) are rotproofing agents for cellulosic products. They are especially suitable for addition to aqueous slurries of cellulosic products. Thus phenylmercuric acetate is dissolved in a solution containing 70% by wt. of methoxy-ethylmercuric acetate, 25% methanol and 25% aq. acetic acid. It can be added to the paper pulp, e.g. while the slurry is in the Jordan, or sprayed on to the paper sheet.

C.O.C.

**Gas-fume-fading Inhibitors**

General Aniline

USP 2,706,142

Compounds of formula—



( $R^1 = \text{Alk of 4-12 C}$ ;  $R^2 = \text{benzene, naphthalene or diphenyl}$ ;  $A = \text{ethylene or propylene}$ ;  $R^3$  and  $R^4 = \text{Alk, Ar, cycloAlk, aralkyl, hydroxyalkyl or atoms to complete a heterocyclic ring, e.g.}$



are gas-fume-fading inhibitors applicable in the dyebath. They are fast to light, washing and dry cleaning.

C.O.C.

**Size for Paper Stock**

Shell Development Co.

USP 2,705,205

The acid-free cyclic components removed from petroleum oils during refining, can be used as a size in the beater without addition of rosin if a paraffin wax of m.p. 155-170°C. has been added to them.

C.O.C.

New Products developed since November 1954—Alphabetical List (IV below)

**IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS****New Products developed since November 1954—Alphabetical List**

Amer. Dyestuff Rep., 44, 837-863, 802 (5 Dec. 1955)

**Absorption Spectra and Stability of Complex Ions**

R. J. P. Williams

J.C.S., 9-15 (Jan. 1956)

**Thermochromism of Compounds containing the Thiocarbonyl and Disulphide Functions**

J. C. D. Brand and J. R. Davidson

J.C.S., 15-22 (Jan. 1956)

Thiocarbonyl compounds and aryl disulphides are weakly thermochromic, and the spectra of certain representative opd., e.g. methyl 1-dithionaphthoate in ethyl oxalate and di(benzothiazol-2-yl) disulphide in anisole (I), have been measured in the temp. range 20-115°C. The visible thermochromism of the thiocarbonyl opd. is associated with the first ( $N \rightarrow A$ ) electronic absorption band, which broadens at high temp. and moves slightly (100-150  $\text{cm}^{-1}$ ) to lower frequencies. The broadening is attributable to the change with temp. of the relative population of the lower vibrational levels of the ground state; this frequency shift is a new effect, explained by a diminution of solvent-solute interaction with rising temp. Di-1-thionaphthoyl disulphide obeys Beer's law at 100°C. and then slowly decomposes. The thermochromism (to 100°C.) of I is due to broadening of the spectrum, and not to reversible dissociation into radicals. The results are probably of wider application, since most coloured substances change colour on warming.

H.H.H.

**Nitryl Borofluoride as a Nitrating Agent**

G. Oláh and S. Kuhn

Chem. and Ind., 98 (28 Jan. 1956)

Nitryl borofluoride (I) is sufficiently stable to effect the nitration of numerous opd., including benzene, toluene, fluorobenzene, chlorobenzene, nitrobenzene, and 1:4-dichloro-2-fluorobenzene. Good yields are obtained, in accordance with the equation—



Paraffins and other aliphatic opd. also are nitrated by I. An electrophilic nitrating mechanism through the  $\text{NO}_2$  cation of I is directly proved.

J.W.D.

**Reaction of Sulphonation****XXVII—Equilibrium between Polysulphonic Acids and their Acid Chlorides**

A. A. Sprýskov and Yu. L. Kuz'mina

Sbornik statei po obshchei khim., 1, 559-563 (1953)

*m*-Benzenedisulphonic acid is dissolved in various mixtures of  $\text{H}_2\text{SO}_4$  and  $\text{HO-SO}_2\text{Cl}$ . Reaction occurs with conversion of one  $\text{SO}_3\text{H}$  group only into  $\text{SO}_2\text{Cl}$ , equilibrium being attained within 3 hr. at 80°C. (equilibrium const. 1.33). Similar data are given for equilibrium mixtures formed by reaction of 1:3:5-naphthalenetrisulphonyl trichloride in similar acid mixtures.

**XXVIII—Preparation and Properties of 1:3-Naphthalenedisulphonic Acid and its Derivatives**

A. A. Sprýskov and O. S. Ivanova

Ibid., 564-567

**XXIX—Relative Activities of Sulphonating Agents**

A. A. Spryskov

*Ibid.*, 2, 878-881 (1953)

Naphthalenetrisulphonyl trichlorides (at 150-170°C.) and 1:5-naphthalenedisulphonyl dichloride (at 100°C.) are sulphonated with various agents, which are found to form the following series, in order of diminishing activity—55% oleum > 73% oleum > SO<sub>3</sub> > HO-SO<sub>3</sub>Cl > H<sub>2</sub>SO<sub>4</sub>.

**XXX—Mechanism of the Hydrolysis of Sulphonic Acids**

A. A. Spryskov and N. A. Ovsyankina

*Ibid.*, 882-886

Existing hypotheses on the mechanism of hydrolytic desulphonation do not account for the observed behaviour under all conditions. It is considered that the process occurs in two stages—(1) formation of an intermediate complex between R-SO<sub>3</sub>H and H<sub>2</sub>O<sup>+</sup>, and (2) reaction of this cation with a base (in the Brønsted-Lowry sense), such as HSO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, with formation of RH. The second stage is rate-determining, and the rate depends on the properties and the concn. not only of the sulphonic acid, but also of the "base". These views are supported by the results of previous experiments on the hydrolysis of naphthalenesulphonic acids in presence of sulphuric, hydrochloric, and phosphoric acids and by the results of further experiments, now described, on the hydrolysis of 1-naphthalenesulphonic and sulphosalicylic acids in presence of acetic acid and the hydrolysis of 4-chloro-1-naphthalene-, *p*-chlorobenzene-, and *p*-bromobenzene-sulphonic acids in presence and in absence of sulphuric or hydrochloric acid.

**XXXVI—Sulphonating Activity of Oleum**

A. A. Spryskov

*J. Gen. Chem. U.S.S.R.*, 25, (9), 1731-1733 (Sept. 1955)

1:3:5-Naphthalenetrisulphonyl trichloride is sulphonated at 84°C. and at 125°C. with various amounts of sulphur trioxide and of oleum containing 9-80% of free SO<sub>3</sub>. It is found that, as the free-SO<sub>3</sub> content of the oleum increases to 33-42%, its sulphonating activity rises to a maximum, after which it falls. Under these conditions the main sulphonating agent appears to be the H<sub>2</sub>SO<sub>4</sub><sup>+</sup> ion.

A.E.S.

**Monosulphonation of β-Naphthol**

H. Iida and M. Ohkawa

*Reports Govt. Chem. Ind. Research Inst. Tokyo*, 50, 391-397 (Dec. 1955)

The monosulphonation of β-naphthol has been studied under various conditions, and the isomers of the reaction products were determined by infrared spectrometric analysis. The results obtained were as follows—

(1) Reaction temperature had a remarkable influence on the ratio of the yield of each isomer produced. For example, after reaction for 3 hr. at 90°C. 2-naphthol-6-sulphonic acid was the only reaction product; while at 60°C. 2-naphthol-3-sulphonic acid was obtained in maximum yield (about 60%), and the yield decreased on changing the reaction temp. to 55°C. or 65°C.

(2) As the reaction time was lengthened, the yield of 2-naphthol-6-sulphonic acid was generally increased, but the increment depended on the temperature; at a low temperature such as 0-10°C. it was almost negligible, and on raising the temperature it was markedly increased.

(3) The influence of the concentration of sulphuric acid used as sulphonating agent on the ratio of the amounts of the isomers produced was examined at 60°C. using sulphuric acid of 85% and 90%. At the beginning of the reaction, the difference in the ratio depended on the H<sub>2</sub>SO<sub>4</sub> concn., but by lengthening the reaction time, it was decreased. Consequently, it was considered that the influence of H<sub>2</sub>SO<sub>4</sub> concn. was small.

AUTHORS

**Mechanism of the Conversion of Naphthalene-1-sulphonic Acid into Naphthalene-2-sulphonic Acid**

S. E. Shol', Ya. K. Sfirkin, V. I. Yakerson, and L. A. Blyumenfeld

*Doklady Akad. Nauk S.S.S.R.*, 101, 1075-1078 (21 April 1955)

The conversion of naphthalene-1-sulphonic acid into naphthalene-2-sulphonic acid at 160°C. is studied with the aid of <sup>35</sup>S-labelled sulphonic acids and sodium sulphate;

sulphate is separated from the sulphonates in the neutralised reaction mixture by chromatography, and the proportions of the isomers are determined by ultraviolet absorption spectrometry. In glycerol and in 85% orthophosphoric acid, no isomerisation occurs. In 78% sulphuric acid isomerisation occurs very readily and proceeds mainly, if not entirely, via the medium (i.e. hydrolysis and re-sulphonation), but in 94% sulphuric acid reaction does not occur so readily and its course is more complex—only 8% conversion occurs via the medium, whereas the total extent of the conversion is 15%. However, these results do not provide unequivocal proof of the occurrence of intramolecular rearrangement.

A.E.S.

**Replacement of the Sulpho Group by Hydroxyl in Aromatic Compounds. I—Reactivity of the Sulpho Groups of Aromatic Compounds in Alkaline and Acid Hydrolysis**

M. Ya. Ilyukovich

*Sbornik statei po obshchei khim.*, 2, 1509-1513 (1953)

A discussion of the behaviour of the sulpho groups of aromatic cpd. when treated with alkaline and acid reagents is illustrated by the known behaviour of various sulphonic acids and by some new data obtained by the author; these observations are interpreted with the aid of electronic theory. When pure reactants are used and catalysts are absent, the alkaline fusion of benzenesulphonic acid proceeds entirely in the direction of the formation of phenol ("alkaline hydrolysis"), which can be obtained in almost theoretical yield; the low yield often obtained is due to further reaction of the phenol, and not to the occurrence of "acid hydrolysis" (formation of hydrocarbon and sulphite). Introduction of OH into benzenesulphonic acid, particularly in the *ortho* and *para* positions, facilitates acid hydrolysis and renders alkaline hydrolysis more difficult. For some compounds the "normal" behaviour is reversed, "acid hydrolysis" being brought about by alkali, and *vice versa*. More frequently, the sulphonic acid is stable to alkali and is converted by acid into the hydroxy cpd. (e.g. pyrrole-2-sulphonic acid and similar cpd. in which there is an unshared pair of electrons on the atom adjacent to the C carrying the sulpho group).

A.E.S.

**Fluorination with Nitrosyl Tetrafluoroborate**

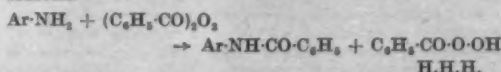
U. Wannegat and G. Hohlstein

*Chem. Ber.*, 88, 1839-1846 (Dec. 1955)**Oxidation of Aromatic Primary Amines with Benzoyl Peroxide**

J. T. Edward

*J.C.S.*, 222-223 (Jan. 1956)

Although oxidation of *N*-substituted anilines with benzoyl peroxide affords *o*-benzamidophenols in yields of up to 40%, only low yields have now been obtained from the following primary amines: *o*- and *m*-toluidine, 2:4:1- and 2:5:1-xylydine, *p*-bromo-, *p*-chloro-, and 2:4-dichloro-aniline. No phenol was isolated on oxidation of aniline, *p*-toluidine, 2:6:1-xylydine, *p*-anisidine, or 2:4:6-tribromo-aniline. The neutral and the basic fractions from these reactions are complex mixtures, from which the azo cpd. and, in most instances, the *N*-arylbenezamide are obtained by chromatography on alumina. Smaller amounts of more complex coloured products were also separated by chromatography. The formation of *N*-arylbenezamides indicates that benzoyl peroxide, besides reacting with amines by a free-radical mechanism, undergoes the heterolytic reaction—

**Mannich Bases as Intermediates in Reactions with Formaldehyde**

J. Theenig, H. Zieg, and H. Mayer

*Chem. Ber.*, 88, 1978-1988 (Dec. 1955)

This is demonstrated for the *C*-substitution of indole, antipyrin, and 2-naphthol by -CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-NHR using formaldehyde in presence of aniline or *N*-methylaniline (R = H or CH<sub>3</sub>).

H.E.N.

**8-Hydrazinopurines and Derived Pyrazolones**

H. Priewo and A. Poljak

*Chem. Ber.*, 88, 1932-1937 (Dec. 1955)

**Oxidation of Phenols with Copper-Amine Catalysts and its Relation to the Mode of Action of Tyrosinase**  
W. Brackman and E. Havinga

**II—Oxidation of Naphthols with Tertiary Amines as Catalysts**

*Rec. Trav. chim.*, **74**, 1021–1039 (Aug.–Sept. 1955)

**III—Kinetics of the Oxidation of Monohydric Phenols with Copper-Morpholine Complex as Catalyst**

*Ibid.*, 1070–1080

**IV—Relations between Hydrogen Peroxide and the Catalytic Oxidation of Phenols**

*Ibid.*, 1100–1106

**V—Reaction Mechanisms**

*Ibid.*, 1107–1118

**Tautomerism. V—Tautomeric Equilibrium, Dimerisation, and Ionisation of Quinone Monoximes (Nitrosophenols)**

A. Schors, A. Kraaijeveld, and E. Havinga

*Rec. Trav. chim.*, **74**, 1243–1261 (Oct. 1955)

Benzoquinone monoxime and chloroquinone monoxime in alcoholic soln. show evidence (absorption spectra) of existing as nitrosophenols. Naphthaquinone and anthraquinone monoximes, however, appear to exist almost completely in the quinonoid form. The spectra of nitroso compounds and complications due to dimerisation are discussed. A.J.

**Separated Chromophoric Systems. XXXI—Comparative Study of the Absorption Spectra of Arylamides of 2:4-Dinitrophenylacetic, 2:4-Dinitrohydrocinnamic, and 4-(2:4-Dinitrophenyl)butyric Acids**

E. A. Smirnov

*J. Gen. Chem. U.S.S.R.*, **25**, (13), 2532–2538 (Dec. 1955)

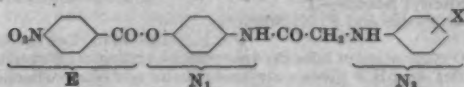
The previous communication (see *J.S.D.C.*, **72**, 112 (March 1956)) refers to visual examination and reflection spectrometry of powders of the title cpd. Absorption spectra of soln. of these dinitro cpd. are now determined, and the results, compared among themselves and with the corresponding reflection spectra, are in the main analogous to those obtained for the mononitro cpd. (see *J.S.D.C.*, **71**, 622 (1955)). A.E.S.

**Compounds containing Two Nucleophilic Systems. I—Colour Phenomena in Derivatives of *p*-(Anilinoacetamido)-*O*-*p*-nitrobenzoylphenol**

E. A. Smirnov

*Sbornik statei po obshchei khim.*, **2**, 1394–1410 (1953)

A study is made of the preparation and properties (including reflection spectra of solid cpd. and absorption spectra of alcoholic soln.) of cpd. of formula—



(X is H, *o*-, *m*-, or *p*-CH<sub>3</sub>, *o*-, *m*-, or *p*-O-CH<sub>3</sub>, *m*-OH, or *m*-N(CH<sub>3</sub>)<sub>2</sub>; N<sub>1</sub> and N<sub>2</sub> denote nucleophilic systems, defined as conjugated systems of double bonds attached to nucleophilic groups; and E denotes an electrophilic system—a conjugated system attached to an electrophilic group). In these cpd. the two systems N<sub>1</sub> and N<sub>2</sub> are separated by CO-CH<sub>2</sub> and are not conjugated with the chromophoric system E. The nucleophilic properties of the system N<sub>1</sub>, which is adjacent to E, are greatly weakened by the substitution of CO in the electron-donating groups OH and NH<sub>2</sub>. On the basis of the simple conjugation theory of colour, neither this system, nor the more powerful system N<sub>2</sub> (which is far removed from E) should have a great effect on the colour of the cpd., which would, in fact, be expected to be colourless. However, on the basis of the theory developed by this school of investigators (formation of "exo" bonds, see *J.S.D.C.*, **67**, 198 (1951); **68**, 464 (1952))—according to which direct interaction between systems of types N and E can occur under suitable conditions and can lead to intense absorption of visible light—these cpd. can be expected to be coloured, particularly in the solid state. All the cpd. are deeply coloured (orange to dark red) in the powder form (when X = H or *m*-OH, the cpd. can be obtained in two crystalline forms—one deeply coloured, and the other only slightly coloured). The colour is deepest when X is in the *para* position; the powerful electron-

donating group N(CH<sub>3</sub>)<sub>2</sub> is the only group that produces an appreciable bathochromic effect when substituted in the *meta* position; and substitution in the *ortho* position has only a slight effect, which may be in either direction. The colour is attributed mainly to interaction between E and N<sub>1</sub>, and experiments on compounds in which only E and N<sub>1</sub> are present indicate that the influence of N<sub>1</sub> is appreciable only when X = H. These interactions are only slight at the low concn. used in the absorption-spectrum experiments, absorption being almost entirely confined to the ultraviolet region except when X = N(CH<sub>3</sub>)<sub>2</sub>, when the soln. is appreciably coloured. A.E.S.

**Kinetics and Mechanism of Diazotisation. IX—Kinetics of Diazotisation in Nitric and in Perchloric Acid**

H. Schmid and A. F. Sami

*MA. Chem.*, **86**, 904–911 (Dec. 1955)

With concentrations of these acids > 0.5 M, there must be added to the right-hand side of the equation—

$$\frac{d(\text{C}_6\text{H}_5\text{N}_2^+)}{dt} = \frac{k_1[\text{C}_6\text{H}_5\text{NH}_2][\text{HNO}_3]^2}{k_2[\text{H}^+] + [\text{C}_6\text{H}_5\text{NH}_2]}$$

$$\text{a term } \kappa[\text{C}_6\text{H}_5\text{NH}_2][\text{HNO}_3] \frac{m^{\frac{1}{2}}\gamma^{\frac{1}{2}}}{a_{\text{H}_2\text{O}}}$$

(*m* = molality, *γ* = activity coefficient of the acid, and *a*<sub>H<sub>2</sub>O</sub> = activity of the water). At 0°C. *κ* is 5.4 for nitric and 4.0 for perchloric acid. Above 1.0 M, the new term becomes dominant. H.E.N.

***o*-Mercapto-azo Compounds**

**VIII—Preparation and Debenzylation of 2-Benzylthio-2'- and -4'-nitroazobenzene**

A. Burawoy, A. Chaudhuri, and C. E. Vellins

*J.U.S.*, **90**–95 (Jan. 1956)

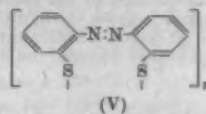
2-Benzylthio-2'- and -4'-nitroazobenzene (I and II) are prepared by the condensation in acetic acid of *o*-benzylthioaniline with *o*- and *p*-nitroazobenzene respectively. I when heated with HBr gives only 2-nitroazobenzene-2'-sulphenyl bromide, which indicates either that the starting material is unable to serve as a hydrogen acceptor or that its debenzylation is faster than the dehydrogenation of the thiol. II, however, gives not only 4-nitroazobenzene-2'-sulphenyl bromide (III) but also a 30% yield of *p*-nitroaniline, indicating a split of III by HBr in preference to its rearrangement. Both I and II yield almost quant. the corresponding stable sulphenyl bromides and tribromides when heated with 1 mol. and with an excess, respectively, of Br<sub>2</sub> in acetic acid.

**IX—Debenzylation of 1-Benzylthio-2-phenylazonaphthalene**

A. Burawoy, A. Chaudhuri, and W. I. Hyslop

*Ibid.*, **96**–99

Debenzylation of 1-benzylthio-2-phenylazonaphthalene (IV), by heating with 1 and 2 mol. of Br<sub>2</sub> in acetic acid, yields almost quant. 2-phenylazonaphthalene-1-sulphenyl bromide and tribromide respectively. With Na in liq. NH<sub>3</sub>, IV is easily debenzylated, forming either the disulphide or (in presence of excess of Na) the Na salt of 1-mercapto-2-phenylazonaphthalene; 2-benzylthioazobenzene, however, is unaffected, whilst 2:2'-dibenzylthioazobenzene, depending on the amount of Na used, gives the polysulphide (V) or the Na salt of 2:2'-dimercaptoazobenzene.



H.H.H.

**Solubilities of Direct and Acid Dyes**

B. N. Mel'nikov and P. V. Mor'ganov

*Kolloid. zhur.*, **17**, 99–106 (1955)

*Chem. Abs.*, **49**, 9031 (25 July 1955)

Solubility determinations are made on purified dye preparations containing 82–88% of dye, 8–15% of water, and 1.5–6.1% of impurities. At all temperatures (70°C. is the highest temp. referred to in *Chem. Abs.*) the solubility of Chrysophenine (I) in water depends on the amount of dye taken for a given vol. of water, and below 45°C. the solubility of Benzopurpurin 10B (II) is also dependent on



the amount of dye taken. It is considered that I and II form colloidal particles under these temp. conditions. The solubilities in water of II above 45°C., of Methyl Orange, Direct Blue, Acid Orange, and Acid Brilliant Orange G at all temperatures, and of I in a 1:9 pyridine-water mixture at 25°C. are independent of the amount of dye. Addition of salts having no common ion raises, and addition of salts having a common ion lowers, the solubilities of some dyes. A.E.S.

#### Effect of Steric Factors on the Properties of Dyes derived from Diphenyl. I—Disazo Dyes derived from Benzidine and from 2-, 2:2', and 3:3'-Substituted Benzidines

B. M. Krasovitskii and D. G. Pereyaslova

*Ukrain. khim. zhur.*, 20, 646-660 (1954)

*Chem. Abs.*, 49, 15242 (10 Nov. 1955)

The results of this work have been described elsewhere (see J.S.D.C., 71, 193 (1955)). A.E.S.

#### 2:2'-Diaminodiphenyl and 2- and 4-Aminodiphenylamine in the Products of Benzidine Rearrangement

M. Večera, J. Petránek, and J. Gasparič

*Chem. and Ind.*, 99 (28 Jan. 1956)

Rearrangement of hydrazobenzene in aq. HCl yields benzidine, diphenylamine, 2:2'-diaminodiphenyl, 2-amino-diphenylamine, and 4-aminodiphenylamine. Recently developed sensitive methods of detection, isolation, and estimation have been used; these are referenced.

J.W.D.

#### Relationship between the Absorption Spectra and the Chemical Constitution of Dyes. Some Effects of Polar Groups, Insulating Links, and Steric Non-coplanarity on the Absorption Spectra of Unsymmetrical Trisazo Benzidine Dyes

R. J. Morris, F. R. Jensen, and T. R. Lusebrink

*J. Org. Chem.*, 19, 1306-1315 (1954)

*Chem. Abs.*, 50, 269 (10 Jan. 1956)

The absorption spectra were measured of two unsymmetrical benzidine dyes, C.I. 581 and 593, and of their closely related, structurally insulated, counterparts and their corresponding exact half-structures. The amount of interaction between chromophoric groups in 95% ethyl alcohol was relatively small, even without structural restrictions, showing a non-coplanar arrangement.

C.O.C.

#### Interaction of Crystal Violet Carbinol and Acids in Organic Solvents

G. Porod, I. Porod, and M. Rebeck

*Mh. Chem.*, 86, 796-818 (Oct. 1955)

#### Ultraviolet and Infrared Spectra of Certain Terphenyls

J. Dorkosch and F. Langer

*Mh. Chem.*, 86, 924-936 (Dec. 1955)

#### Dyes having Antipyrin Nuclei. V—Hydrolysis of Dyes having *ortho* Substituents

O. F. Ginsburg and D. V. Ioffe

*J. Gen. Chem. U.S.S.R.*, 25, (9), 1739-1743 (Sept. 1955)

It has been shown previously (cf. J.S.D.C., 70, 306 (1954); 71, 473 (1955)) that the introduction of *para* substituents into the phenyl nucleus of diantipyrinylmethane dyes greatly affects the hydrolysis const.—*para* electron-donating substituents decrease the hydrolysis of the dye (i.e. increase the dissociation of the carbinol form), and *para* electron acceptors increase the hydrolysis. It is now shown that *ortho* substituents—both electron donors and electron acceptors—always decrease the hydrolysis of the dye. A.E.S.

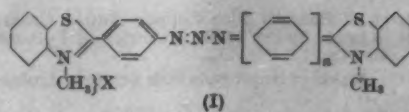
#### Azacyanines—II

A. I. Kiprianov, V. Ya. Poshinok, and A. I. Tolmachev

*Ukrain. khim. zhur.*, 20, 204-210 (1954)

*Chem. Abs.*, 49, 12834 (25 Sept. 1955)

Numerous reactions are carried out with 2-amino- and 2-*p*-aminophenyl-benzothiazole and their deriv. Various diazoamino epd. (triazons) are prepared and characterised, their absorption max. in soln. being given. The azo dye (azastylene) obtained by coupling diazotised 2-*p*-aminophenyl-3-ethylbenzothiazolium chloride with *NN*-dimethylaniline has  $\lambda_{\max}$  474 m $\mu$ . (alcohol). Two triazacyanines (I) are prepared—I (*n* = 0) has  $\lambda_{\max}$  440 m $\mu$ . (alcohol), and I (*n* = 1) is very unstable and has  $\lambda_{\max}$  510-520 m $\mu$ . (alcohol).



(I)

A.E.S.

#### Cyanine Dyes. VIII—Some 5:5'- and 6:6'-Di-substituted Thiocarbocyanines

I. I. Levkoov, V. G. Zhiryakov, N. N. Sveshnikov, and N. S. Barvyn'

*Sbornik statei po obshchei khim.*, 2, 1263-1272 (1953)

5- and 6-Allyloxy-, 5- and 6-benzyloxy-, 5- and 6-ethoxycarbonylmethoxy-, 6-phenoxy-, and 6-carboxymethoxy-2-methylbenzothiazoles are prepared and converted via their quaternary salts into a series of new thiocarbocyanines. It is found that the substitution of various groups in the methoxy groups of 5:5'- and 6:6'-dimethoxy-thiocarbocyanines has only a very slight effect on the positions of their absorption maxima. A.E.S.

#### Trinuclear Sensitising Dyes. IV—Dinuclear Dyes as By-products

Y. Hishiki

*Repts. Sci. Research Inst. (Japan)*, 30, 39-47 (1954)

*Chem. Abs.*, 50, 93 (10 Jan. 1956)

In the condensation of 2-methylbenzoxazole and 2-methylbenzothiazole methiodides or ethiodides in presence of  $\text{HC}(\text{O}_2\text{C}_2\text{H}_5)_2$  alone or with  $\text{Cl-CH}_2\text{-COOH}$  or  $\text{Cl-CH}(\text{COOH})_2$  to trinuclear dyes a number of dinuclear dyes, a list of which is given, were obtained as by-products. C.O.C.

#### o-Quinones—VIII

L. Horner and K. Sturm

*Annalen*, 597, 1-19 (Dec. 1955)

Addition reactions of, diene syntheses with, and dimerisation of 4:5-dimethylbenzo-o-quinone are described. H.E.N.

#### Reaction between Quinones and Anthranilic Acids

R. M. Acheson and B. F. Sansom

*J.C.S.*, 4440-4443 (Dec. 1955)

Quinone reacts with anthranilic acid (2 mol.) and its deriv. to give the corresponding 2:5-dianilinoquinones, some of which may be cyclised by  $\text{H}_2\text{SO}_4$ . Monoanilinoquinones were not isolable from these reactions, although 2:3-dimethoxy-*p*-benzoquinone combined with anthranilic acid, but not with its methyl ester or *N*-methyl deriv., to give 5-*o*-carboxyanilino-2:3-dimethoxy-*p*-benzoquinone; the hydroxyl groups of the quinol, obtained on catalytic reduction, did not react with diazomethane. H.H.H.

#### Synthetic and Oxidative Studies in the Polyhydroxydiphenyl Series—I

J. M. Bruce and F. K. Sutcliffe

*J.C.S.*, 4435-4440 (Dec. 1955)

Oxygenation of 2:3-dihydroxydiphenyl (I) in a phosphate buffer at pH 8 gives only amorphous material, whereas treatment with silver oxide in dry ether yields deep brown 2:3-diphenylbenzoquinone. Similarly, 3:4-dihydroxydiphenyl affords deep reddish-brown 3:4-diphenylbenzoquinone. Oxidation of 2:3:4-trihydroxydiphenyl (III) in aqueous dioxan with sodium iodate gives a golden-orange compound believed to be 2':3':4':4'-tetrahydroxy-1':5'-diphenylbenzocycloheptatrien-3-one. I and III are prepared from organometallic compounds and cyclohexanone. H.H.H.

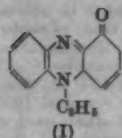
#### Absorption Spectra and Structure of *N*-Alkylphenazinones

Yu. S. Rozum

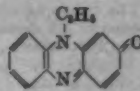
*Sbornik statei po obshchei khim.*, 1, 600-606 (1953)

When *N*-alkylphenazinones (e.g. I and II) are treated with acid, they are converted into quaternary salts of phenazinols (1- and 2-, respectively), the absorption spectra of which characterise the positions of the OH groups, and therefore of the CO groups of the original epd. The absorption spectra of quaternary salts of methoxyphenazines are almost identical with those of the corresponding phenazinol salts. Spectroscopic investigation of these and other phenazine deriv. provides data which are applied in the identification of oxidation products yielded by various phenazine deriv. The structures of four new *N*-alkylphenazinones are established, viz. 4-ethoxy-II, 6-ethoxy-II, 1:6-diethoxy-II, and 3-ethoxy-6-methoxy-II (Chem. Soc. numbering).





(I)



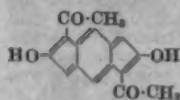
(II) A.E.S.

### Interaction of Acetylacetone, Benzoquinone, and Pyridine

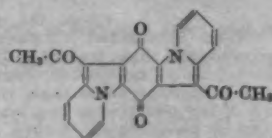
A. M. Islam and R. A. Raphael

*Chem. and Ind.*, 1635-1636 (10 Dec. 1955)

The structure I assigned to the coloured product of interaction of acetylacetone, benzoquinone, and pyridine by Ionescu (*Bull. Soc. chim. France*, 41, 1094 (1927)) is shown to be incorrect since the compound contains nitrogen. Structure II is proposed as an alternative. The compound gives intense violet solutions in diethyl malonate and diethyl phthalate.



(I)



(II)

A.J.

### Chlorine-substituted Copper Phthalocyanine

Y. Banaho

*Reports Govt. Chem. Ind. Research Inst. Tokyo*, 50, 354-360 (Nov. 1955)

When copper phthalocyanine purified with conc.  $H_2SO_4$  is treated with aromatic solvents, its crystal structure is transformed, and it grows to a long needle-like crystal. This reduces the value of copper phthalocyanine as a pigment. An attempt has been made to obtain a pigment stable in solvents by introducing chlorine atoms into the copper phthalocyanine molecule by treatment with anhyd.  $AlCl_3-NaCl$  chlorination either with anhydrous phthalic acid [sic] or with trichlorobenzene, and synthesis from anhydrous chlorophthalic acid by the urea method.

Study of the properties of the blue pigments thus obtained gave the following results—(1) The more chlorine atoms were introduced, the greener became the colour of the pigments. The acidity of the solvents used in chlorination also affected the colour of the pigments. (2) Introduction of one or two chlorine atoms into a copper phthalocyanine molecule made the pigments stable in aromatic solvents. (3) X-Ray reflection indicated that the substituted copper phthalocyanine did not change its crystal structure when boiled with xylene. AUTHOR

### New Synthesis of Chrysene

A. D. Jarrett and J. D. Loudon

*J.C.S.*, 4052-4054 (Dec. 1955)

### Synthesis of Highly Condensed Ring Systems. X—Clar's Terrylene and Dibromoterrylene

A. Zinke, H. Nussmüller, and R. Ott

*Mh. Chem.*, 86, 853-858 (Oct. 1955)

Clar (*Chem. Ber.*, 51, 52 (1918)) prepared what he considered to be terrylene and its 3:11-dibromo deriv. (I) by  $NaCl-AlCl_3$  fusion of perylene and 1-bromonaphthalene. I, however, does not contain bromine and is separable into three hydrocarbons, one of which is shown probably to have the formula II by synthesis from 3:9-dibromo- or 3:4:9:10-tetrachloro-perylene and naphthalene. II is also obtained, together with other opd., by  $NaCl-AlCl_3$  fusion of perylene and naphthalene.



(II)

H.E.N.

### Polynuclear Heterocyclic Systems. IX— $n-\pi^*$ Transitions in the Spectra of Aromatic Aza-hydrocarbons

G. M. Badger and I. S. Walker

*J.C.S.*, 122-126 (Jan. 1956)

The ultraviolet spectra of quinoxaline, pteridine, 1:2:5:6-dibenzophenazine, 1:4-diphenylphthalazine, 1:2-benzo-

phenazine, 3:4-benzocinnoline, 1:4-diazatriphenylene, 5:6:11:12-tetra-azannaphthacene, and 3:4:5:6-dibenzocinnoline have been examined in both ethanol (polar solvent) and cyclohexane or carbon tetrachloride (non-polar solvents). Three main regions of absorption, similar to those given by the corresponding aromatic hydrocarbons, are generally obtained. In the long-wavelength region many of the aza compounds show an additional absorption region (particularly in non-polar solvents), which is held to be due to a transition involving the promotion of a non-bonding electron from the N atom to an unfilled  $\pi$  orbital ( $n-\pi^*$  transition). H.H.H.

### Colour Reactions of Condensed Polycyclic Aromatic Hydrocarbons and their Related Quinones in Solutions of Concentrated Sulphuric Acid

T. Handa

*Bull. Chem. Soc. Japan*, 28, 483-489 (Sept. 1955)

The absorption spectra of a number of polynuclear hydrocarbons and quinones have been measured in soln. of  $H_2SO_4$  of different concn. A family of curves is obtained for each compound which, after adjustment for solvent effect, show one or more isosbestic points. From these the basicities of the compounds  $pK_b$  are obtained by Hammett's method (L. A. Flexner, L. P. Hammett, and A. Dingwall, *J. Amer. Chem. Soc.*, 57, 3103 (1935)). A.J.

### Dyes for Acetate Rayon

Y. Banaho

#### I—Dyeing Properties and Preparation of $\beta$ -Hydroxyethylaminoanthraquinones

*Reports Govt. Chem. Ind. Research Inst. Tokyo*, 50, 328-332 (Oct. 1955)

$\beta$ -Hydroxyethylaminoanthraquinones have good properties as dyes for acetate rayon. Twenty-one aminoanthraquinones and derivatives were synthesised and their dyeing properties were tested, with the following results—

(1) When  $\beta$ -hydroxyethylamino groups are introduced into the anthraquinone nucleus the dyes become readily dispersible in water, but the affinities for cellulose acetate might not depend upon the number of this substituent.

(2) The dyes which are substituted with one  $\beta$ -hydroxyethylamino group and another amino group in the 1:4 position of the anthraquinone nucleus were found to have good dyeing properties.

(3) 1- $\beta$ -Hydroxyethylaminoanthraquinone, 1-amino-4- $\beta$ -hydroxyethylaminoanthraquinone, 1:4-bis-( $\beta$ -hydroxyethylamino)-anthraquinone, 1:4-bis-( $\beta$ -hydroxyethylamino)-5:8-dihydroxyanthraquinone, 1-methylamino-4- $\beta$ -hydroxyethylaminoanthraquinone, and 1- $\beta$ -hydroxyethylamino-4- $p$ -aminoanilinoanthraquinone have potential uses as dyes.

#### II—Synthesis of 1:4-Bis-( $\beta$ -hydroxyethylamino)-anthraquinones

*Ibid.*, 332-336

Quinizarin (100 g.), recryst. from monochlorobenzene, was dispersed in water (2 litres), anhyd.  $Na_2CO_3$  (100 g.) added, and the dispersion treated with hydrosulphite (60% purity, 200 g.) at 80°C. with stirring for 1 hr. under  $N_2$ . The two isomers of leuco-quinizarin (I) were prepared and their properties compared.

Treatment of I (4.84 g.) dispersed in water (24 c.c.) with monoethanolamine (7.2 g.) followed by boiling for 8 hr. gave leuco-1:4-bis-( $\beta$ -hydroxyethylamino)-anthraquinone (II) (6.08 g.), of m.p. 225-226°C. Reaction of II with  $SOCl_2$  at 140-150°C. for 15 min. in nitrobenzene gave blue-violet crystals, m.p. 238-239°C.

1:4:5:8-Tetra-aminoanthraquinone (15 g.) was treated with hydrosulphite (60% purity, 37.5 g.) in water (320 c.c.) and  $NaOH$  (27 g.) at 102°C. for 2-3 hr. The leuco-1:4:5:8-tetrahydroxyanthraquinone thus obtained (4.0 g.) was added to a mixture of water (30 c.c.),  $\beta$ -hydroxyethylamine (6.0 g.), and ethyl alcohol (3 c.c.), and treated with hydrosulphite (1 g.) at 60°C. for 3 hr.; 4.2 g. of a compound which gave a reddish-brown solution in 1-butanol was obtained. This opd., heated at 130°C. for 15 min. in nitrobenzene (10 g.) and  $SOCl_2$  (0.1 c.c.), gave 1:4-bis-( $\beta$ -hydroxyethylamino)-5:8-dihydroxyanthraquinone (3.58 g.), a green-blue dye, of m.p. 220°C. recryst. from monochlorobenzene, which is presumably similar to Celliton Fast Blue Green B.

### III—Synthesis of Unsymmetrically Substituted 1- $\beta$ -Hydroxyethylaminoanthraquinones

*Ibid.*, 337-340

1- $\beta$ -Hydroxyethylamino-4-methylaminoanthraquinone (25.2 g.), of m.p. 170°C., was obtained by heating a mixture of leuco-quinizarin (24.2 g.), 30% methylamine (15.1 g.),  $\beta$ -hydroxyethylamine (6.72 g.), and butyl alcohol (190 g.) at 95°C. for 8 hr., steam-distilling, and purifying with 20% HCl and chlorobenzene. This blue dye was found to be similar to Cellulose Brilliant Blue B from analysis and spectrophotometric comparisons.

Leuco-quinizarin (24.2 g.) dispersed in water (120 c.c.) was treated with  $\beta$ -hydroxyethylamine (16.3 g.) and *p*-phenylenediamine (32.7 g.) at 100°C. for 12 hr.; the product was dissolved in nitrobenzene (109 g.), treated with  $\text{SOCl}_2$  (0.5 c.c.) at 150°C. for 30 min., and purified with dilute sulphuric acid to give 1-*p*-aminoanilino-4- $\beta$ -hydroxyethylaminoanthraquinone (24.3 g.), of m.p. 225°C., a blue-green dye for acetate rayon.

### IV—Synthesis of 1-Amino-4-Hydroxyanthraquinone

*Ibid.*, 341-344

The reaction temp., time, and concn. of acetic acid used as catalyst in a new method of preparation were investigated, and suitable reaction conditions were as follows—

Urea (50 g.), leuco-quinizarin (24.2 g.), and acetic acid (18.0 g.) were heated at 110–113°C. in butyl alcohol (250 g.) for 30 hr. with stirring; crude green crystals (24.5 g.) with a metallic lustre were obtained by vacuum distillation. Purification was carried out by heating the product with a large amount of  $\text{H}_2\text{SO}_4$  (50–60%) and adding water. The yield of the purified red epd. (m.p. 215°C.) was 90%. The amount of  $\text{NH}_3$  evolved was measured. It was concluded that 1-amino-4-hydroxyanthraquinone is aminated by  $\text{NH}_3$ , which is produced by the reaction between urea and butyl alcohol.

AUTHOR

### Magnetochemical Study of Violanthrene-Iodine System

Y. Matsunaga

*Bull. Chem. Soc. Japan*, 28, 475–479 (Sept. 1955)

The measured magnetic susceptibility of the violanthrene-iodine complex (assumed to have the molecular ratio 1:2) is significantly less, i.e. more paramagnetic, than the calculated value. Violanthrene-bromine and perylene-iodine and -bromine are similar. Reasons are discussed.

A.J.

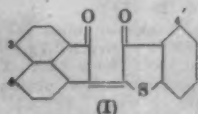
### Condensation of 3:4-Dihalogenoacennaphthenequinones with 2:3-Dihydrothionaphthen-3-one and its Derivatives

A. P. Karishin and T. P. Fedorenko

*Ukrain. khim. zhur.*, 19, 631–638 (1953)

*Chem. Abs.*, 49, 12414 (25 Sept. 1955)

The following derivatives of I (colours not stated) are obtained by condensation of the title epd.—3:4-di-Cl, 3:4-di-Br, 3-Br-4-Cl, 3:4-di-Cl-2:5-di- $\text{NO}_2$ , 3-Br-4-Cl-2:5-di- $\text{NO}_2$ , 3:4:6'-tri-Cl, 3:4-di-Br-6'-Cl, 3-Br-4:6'-di-Cl, 3:4:6'-tri-Cl-2:5-di- $\text{NO}_2$ , 3-Br-4:6'-di-Cl-2:5-di- $\text{NO}_2$ , 3:4-di-Cl-6'- $\text{C}_6\text{H}_5$ -O, 3:4-di-Br-6'- $\text{C}_6\text{H}_5$ -O, 3-Br-4-Cl-6'- $\text{C}_6\text{H}_5$ -O, 3:4-di-Cl-6'- $\text{C}_6\text{H}_5$ -O-2:5-di- $\text{NO}_2$ , 3-Br-4-Cl-6'- $\text{C}_6\text{H}_5$ -O-2:5-di- $\text{NO}_2$ , 3:4:6'-tri-Cl-4'- $\text{CH}_3$ , 3:4-di-Br-6'-Cl-4'- $\text{CH}_3$ , 3-Br-4:6'-di-Cl-4'- $\text{CH}_3$ , 3:4:6'-tri-Cl-4'- $\text{CH}_3$ -2:5-di- $\text{NO}_2$ , 3-Br-4:6'-di-Cl-4'- $\text{CH}_3$ -2:5-di- $\text{NO}_2$ . The following thiophanthren analogues of I are prepared—3:4-di-Cl, 3:4-di-Br, 3-Br-4-Cl, 3:4-di-Cl-2:5-di- $\text{NO}_2$ , 3-Br-4-Cl-2:5-di- $\text{NO}_2$ . Only the dyes containing nitro groups are readily reduced to the leuco form.



(I)

A.E.S.

### Preparation of Indigo from $\beta$ -Hydroxyethylamine

T. Yamanaka

*Repts. Sci. Research Inst. (Japan)*, 30, 191–195 (1954)

*Chem. Abs.*, 50, 304 (10 Jan. 1956)

$\text{C}_6\text{H}_5\text{NHCH}_2\text{CH}_2\text{OH}$  (I) (from aniline and  $\text{HOCH}_2\text{CH}_2\text{Cl}$ ) was cyclised by alkali fusion ( $\text{NaOH}$ ,  $\text{KOH}$ , or  $\text{CaO}$ ) through indoxyl to give a 92% yield of

indigo. The following conditions proved to be necessary—

(1) presence of Na metal to remove a trace of water from the alkali; (2) commencing by forming the Na salt of I to prevent formation of water and to stabilise the bonds between the C atoms in the side-chain of I; (3) dissolving the fusion mixture in water in a glass vessel at 10°C. and an oxidation to indigo. The weight of alkali used was 20 times that of I; if only half this alkali was used, the yield went down to 74%.

C.O.C.

### Synthesis of pseudoindole Derivatives and Indocyanines. I—4-Nitro-, 4-Amino-, 4-Acetamido-, and 4-Dialkylamino-pseudoindoles. II—6-Acetamido- and 6-Dimethylamino-2:3:3-trimethylpseudoindoles. III—Effect of Substituents in the Benzene Rings of Symmetrical Indocarbocyanines on their Absorption Spectra

E. D. Sych

*Ukrain. khim. zhur.*, 19, 643–651,

652–656, 657–661 (1953)

*Chem. Abs.*, 49, 12429 (25 Sept. 1955)

Various substituted 2:3:3-trimethylpseudoindoles are prepared, and those, treated with orthoformic ester, yield symmetrically substituted bis(1:3:3-trimethyl-2-pseudoindole)trimethincyanine salts, the other substituents in each of the pseudoindole ring systems being ( $\lambda_{\text{max}}$  in  $\text{m}\mu$ , given in parentheses)—4-nitro (542), 4-amino (555), 4-dimethylamino (550), 4-diethylamino (550), 4-acetamido (552), 7-chloro-4-nitro (546), 4-amino-7-chloro (546), 7-chloro-4-methylamino (555), 4-acetamido-7-chloro (553), 7-dimethylamino (550), 6-dimethylamino (568), 6-dimethylamino as quaternary methoperchlorate (546), 6-acetamido (552), 5-dimethylamino (605–608), 5-acetamido (578). The shifts in  $\lambda_{\text{max}}$  resulting from symmetrical disubstitution of  $\text{N}(\text{CH}_3)_2$  in the 4, 5, 6, and 7 positions are +5, +60, +23, and +5  $\text{m}\mu$ , respectively. 6-Amino groups are true auxochromes—their bathochromic effect is increased by alkylation, decreased by acylation, and reduced to zero by salt formation.

A.E.S.

### X-Ray Structure of Indigo and Thioindigo

E. A. Gribova

*Doklady Akad. Nauk S.S.S.R.*, 102,

279–281 (11 May 1955)

Three-dimensional electron-density series are derived from the results of X-ray-diffraction experiments on indigo and are applied in a detailed analysis of the structure of this dye. The general structural pattern, space group, and cell dimensions are identical with those found by von Eller (see *J.S.D.C.*, 68, 361 (1952)), but the values of the atomic co-ordinates are somewhat different. All the atoms of the indigo molecule are in one plane, apart from the N atoms (0.07 Å. out of the plane) and the carbonyl C atoms (0.05 Å. out of the plane). Each N atom is at 2.88 Å. from an O atom of the same molecule and at 0.94 Å. from an O atom of a neighbouring molecule; it is therefore considered that hydrogen bonding occurs. A less detailed examination of thioindigo is made; the results are in accord with those of von Eller (*loc. cit.*).

A.E.S.

### Indigoid Dyes

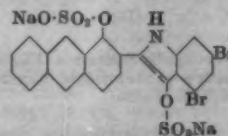
#### IV—New Method of preparing NN'-Alkylated Indigoid Dyes from Commercial Indigoids

R. Pummerer and F. Meininger

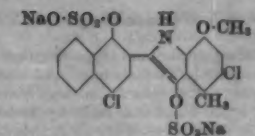
*Annalen*, 590, 173–194 (1954)

*Chem. Abs.*, 50, 301 (10 Jan. 1956)

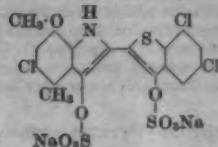
Indigo could not be successfully alkylated, but the leuco sulphuric esters were readily alkylated to yield the leuco esters of NN'-dialkylindigo. These were easily converted to an NN'-dialkylindigo, which, in turn, was partly dealkylated to a monoalkylindigo. Halogenated Indigosols as well as unsymmetrical indigoid dyes, e.g. Indigosol AZG, Anthrasol Printing Blue IGG and IB, were also alkylated. None of the alkylated dyes was suitable for dyeing cotton or wool. The constitutions of the following dyes are given—



Indigosol AZG



Anthrasol Printing Blue IGG

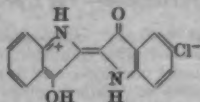


Anthrasol Printing Blue IB

### V—Absorption Spectra of Indigoid Dyes and of their Salts with Acids

R. Pummerer, F. Meininger, G. Schrott, and H. Wagner  
*Ibid.*, 195-216  
*Chem. Abs.*, p. 303

The spectra of indigo (I), *NN'*-dimethylindigo (II), and other indigoid structures have been studied for evidence of the fine structure of the indigo molecule. I, II, and *NN'*-ethylindigo (III) form mono-acid salts with HCl; I forms both mono- and di-acid salts with  $H_2SO_4$ , but only a monoperochlorate with  $HClO_4$ , whereas II and III form diperochlorates. The spectra of the mono-acid salts show shifts to longer wavelengths; this is taken to show that there exists in indigo an *o*-quinonoid system of the type—



The spectra of the diperochlorate of II, 2-benzylidene-pseudindoxyl, and isatin 2-anil in neutral and acid solution also support structures similar to the above.

C.O.C.

### Enzymatic Identification of the Anthocyanin Pigment of Blackberry

H. T. Huang

*Nature*, 177, 39 (7 Jan. 1956)

### Chemistry of Flower Colour in the Dahlia

E. C. Bate-Smith, T. Swain, and C. G. Nordstrom

*Nature*, 176, 1016-1018 (26 Nov. 1955)

### Chemical Constitution of Gamboge

M. Amorosa

*Ann. chim. (Rome)*, 45, 40-49 (1955)

*Chem. Abs.*, 50, 369 (10 Jan. 1956)

An account of work on the degradation products of gamboge.

C.O.C.

### Oxygen-containing Groups on the Surface of Carbon Black

M. L. Studebaker, E. W. D. Huffman, A. C. Wolfe, and L. G. Nabors

*Ind. Eng. Chem.*, 48, 162-166 (Jan. 1956)

The oxygen-containing groups present in various types of carbon black were analysed by treatment with diazomethane followed by determination of methoxy content before and after hydrolysis to provide a measure of the carboxylic and phenolic oxygen. Quinone-type oxygen was estimated by increase in nitrogen content and also by reduction with sodium borohydride. In all samples, approx. 18% of the total oxygen was present in the *p*-quinone form, whilst carboxylic oxygen was approx. 5% in the furnace blacks, 9% in the rubber-grade channel blacks, and 8-10% in the colour blacks (all of which had total O contents > 4%). For every 3.2 O atoms present as carboxyl, 1 O atom was present in phenolic form. The whole of the oxygen was not accounted for. It is considered that rubber properties can be strongly influenced by the presence of these reactive groups in the carbon black.

W.K.R.

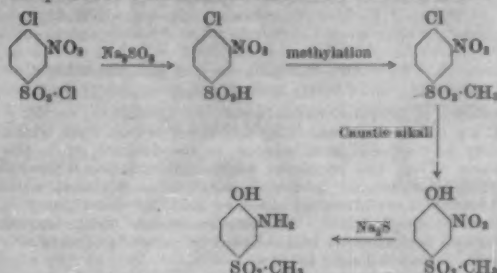
### PATENTS

#### Metal(Cobalt)-complex Monoazo Dyes for Wool, Nylon, etc.

Ciba

BP 743,563

The cobalt complexes of *o*,*o'*-dihydroxymonoazo compounds, free of  $SO_3H$  and  $COOH$  groups but containing a  $CH_2SO_3$  group, in which < 1 Co atom is combined with 1 mol. of monoazo compound, dye wool, nylon, etc. from neutral or weakly acid baths. The preferred monoazo compounds are those obtained by coupling a diazotised methylsulphonyl-*o*-aminophenol with an *ortho*-coupling phenol, naphthol, pyrazolone etc., and the complexes preferably contain substantially 2 mol. of monoazo compound to 1 atom of Co. Thus the series of reactions



give 2-aminophenol-4-methylsulphonylamine, which is diazotised and coupled with 3-methyl-1-phenyl-5-pyrazolone dissolved in aq. NaOH. Heating this monoazo compound for 30 min. at 80-85°C. with aq.  $CoSO_4$  gives the metal complex, which dyes wool yellow-brown from a neutral or acetic acid bath.

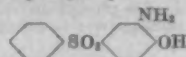
E.S.

#### Metallisable Monoazo Dyes Free from Sulpho and Carboxy Groups

Ciba

BP 743,907

Monoazo dyes made by diazotising a phenyl- or benzylsulphonyl of *o*-aminophenol and coupling with a suitable *ortho*-coupling hydroxy compound, both components being free of sulpho and carboxy groups, may be metallised in substance, on the fibre, or in the dyebath. The Cr and Co complexes containing substantially 2 mol. of monoazo compound to 1 atom of metal dye wool and nylon from neutral or weakly acid baths. Thus 2-chloronitrobenzene-5-sulphonyl chloride is treated with benzene and  $AlCl_3$  at 40-50°C. to give the 5-phenylsulphonyl. Treatment in boiling 10% aq. NaOH then replaces the Cl atom by an OH group, and reduction, e.g. with  $Na_2S$ , converts the  $NO_2$  into  $NH_2$ , giving the phenylsulphonylamine derivative—



This is diazotised and coupled with 5-pyrazolone-3-carboxy-*n*-butylamide, to give the monoazo compound, which dyes wool red by the afterchrome or metachrome process, and can be converted into its Cr complex in substance by boiling with sodium chromosalicylate and NaOH.

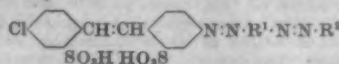
E.S.

#### Copperable, Disazo, Stilbene Direct Dyes

Ciba

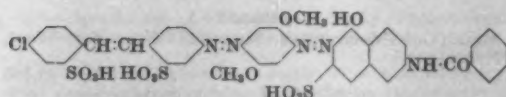
BP 744,406

Disazo compounds—



( $R^1$  = the residue of a middle component;  $R^2$  = the residue of an aminonaphtholsulphonic acid) are direct cotton dyes which may be coppered in substance, in the dyebath, or on the fibre if  $R^1$  and  $R^2$  contain suitable groups in *ortho* positions to the azo link between them. Thus, the amino group in 4-amino-4'-nitrostilbene-2,2'-disulphonic acid is diazotised and replaced by a Cl atom, and the nitro group then reduced to  $NH_2$ . The 4-amino-4'-chlorostilbene-2,2'-disulphonic acid so formed is then diazotised and coupled with 2:5-dimethoxyaniline under acid conditions, and the aminomonoazo compound formed is diazotised and coupled with an alkaline solution of *N*-benzoyl-J acid to give



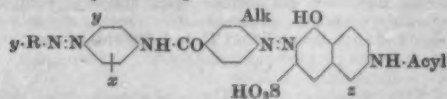


The copper complex is formed by boiling with ammoniacal copper sulphate and ethanolamine, and dyes cotton green-grey. E.S.

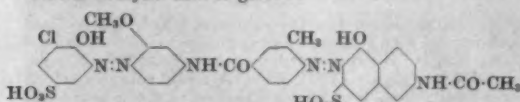
#### Copperable Disazo Direct Dyes

BP 744,229

Disazo compounds of general formula—



( $x = \text{H, Alk, O-Alk, or SO}_3\text{H}$ ; one  $y = \text{OH}$ , the other  $y = \text{OH, OCH}_3, \text{ or COOH}$ ;  $z = \text{H, Hal, or SO}_3\text{H}$ ;  $y\text{-R} =$  radical of benzene, naphthalene, or pyrazolone series,  $y$  being *ortho* to the azo link) are direct cotton dyes which may be coppered in substance, in the dyebath or on the fibre. Thus the monoazo compound 2-amino-6-chlorophenol-4-sulphonic acid  $\rightarrow$  *m*-anisidine is acylated with 3-methyl-4-nitrobenzoyl chloride, and the nitro group is then reduced to  $\text{NH}_2$ . The aminomonoazo compound so formed is diazotised and coupled in presence of soda ash with *N*-acetyl-J acid to give



The copper complex is prepared by boiling with ammoniacal copper sulphate; it dyes cellulose fibres red. E.S.

#### Black Tetrakisazo Direct Dyes

CFM

BP 743,957

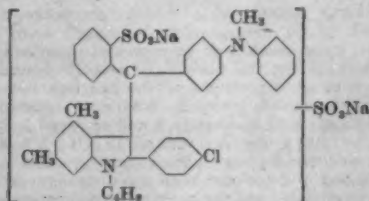
The black, dischargeable direct dyes obtained by coupling tetrazotised 4:4'-diaminodiphenylamine-2-sulphonic acid (I) with 2 mol. of J acid, or 1 mol. of J acid and 1 mol. of a different aminonaphthol sulphonic acid, tetrazotising and coupling with 2 mol. of *m*-phenylenediamine or its derivatives containing no solubilising groups, have better solubility in presence of salt or in hard water than the similar dyes in which *y* acid is used instead of J acid (BP 470,407: J.S.D.C., 53, 438 (1937)) or one of the *m*-phenylenediamine mols. is replaced by a naphthol or aminonaphthol (BP 703,446: J.S.D.C., 70, 203 (1954)). Thus I is tetrazotised and coupled with an alkaline soln. of 2 mol. of J acid, and the product is tetrazotised and coupled with 2 mol. of *m*-phenylenediamine in presence of soda ash. The tetrakisazo dye so formed dyes cotton and rayon reddish-black. E.S.

#### Diphenyl-Indolylmethane Acid Dyes

FH

BP 742,934

Green acid dyes of better perspiration and sea-water fastness than those of BP 495,881 (J.S.D.C., 55, 225 (April 1939)) are made by condensing 4-chlorobenzophenone-2'-sulphonic acid with a 1-alkyl-2-phenyl-indole in conc.  $\text{H}_2\text{SO}_4$  and reacting the product with a monoalkylamino-benzene carrying nuclear alkyl or halogen or an *o*- or *m*-alkoxy group. Thus Na 4-chlorobenzophenone-2'-sulphonate and *N*-isobutyl-2-*p*-chlorophenyl-4:6-dimethyl-indole are added to 20% oleum at 30°C. and stirred for 20 hr. at 20–25°C. After separating by pouring on to ice, the product is heated at 80–85°C. for 2 hr. with mono-methylaniline. The dye—



results by stirring with aq. HCl, filtering, redissolving and adding NaCl. R.K.F.

#### Anthraquinone-Azo Leuco Sulphuric Esters

FH

BP 742,925

Yellow anthraquinone-azo dyes derived by coupling a 2-aminoanthraquinone, which may also carry a 3-halogen atom, with an acetoacetanilide are converted to the corresponding leuco-sulphuric ester by treating them with chlorosulphonic acid, or other  $\text{SO}_3$  yielding agent, in presence of a tertiary base and a metal. Thus the dye obtained from diazotised 2-amino-3-chloroanthraquinone and acetoacetanilide is added with Fe powder to chlorosulphonic acid in pyridine at 35°C. After heating to 50°C. the mixture is run into 5% aq.  $\text{Na}_2\text{CO}_3$  and the pyridine distilled off under reduced pressure. The Fe compounds are filtered off the leuco sulphuric ester salted out.

R.K.F.

#### Leuco-Benzanthrone-Pyrazoleanthrone Sulphuric Esters

ICI

BP 743,865

3-(1-Aminoanthraquinone-2-carboxylamido)-benzanthrone-pyrazoleanthrone is treated with a sulphating agent in the presence of a metal and a tertiary base or organic amide derived from a secondary amine to produce the corresponding leuco sulphuric ester. Alternatively a metal salt of the leuco dye is treated with a sulphating agent and tertiary base or organic amide. Thus 3-(1-aminoanthraquinone-2-carboxylamido)-benzanthrone-pyrazoleanthrone is stirred at 20°C. for 19 hr. in dimethylformamide containing Zn dust and Na  $\beta$ -naphthalene sulphonate in an atmosphere of  $\text{N}_2$ . A dimethylformamide- $\text{SO}_2$  mixture is then added at 0–5°C. and the whole poured into aq.  $\text{Na}_2\text{CO}_3$ . After removing the Zn residues and distilling off the dimethylformamide the sulphuric ester is precipitated by adding NaCl. R.K.F.

#### Quinazoline-Anthrimsides—Vat Dyes

BASF

BP 743,034

Yellow to red primary mono-aminoanthraquinones (2 mol.) are condensed with quinazolines substituted by halogen in the 2 and 4 positions, and in at least one of the 5, 6, 7 or 8 positions to produce yellow to red vat dyes. Thus 1-aminoanthraquinone and 2:4:6-trichloroquinazoline are heated together in nitrobenzene for 2 hr. at 190°C.

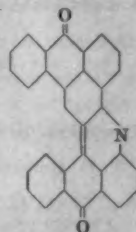
R.K.F.

#### Coeramidonine Pigments

S

BP 743,509

1-*N*-(3'-Benzanthronyl)-aminoanthraquinones are treated with an acid condensing agent, e.g. a metal halide or  $\text{H}_2\text{SO}_4$ , to give the corresponding coeramidonine, which after acid-pasting or grinding is an orange to brown pigment suitable for colouring paper, textile printing, paints, etc. Thus 1-*N*-(3'-benzanthronyl)aminoanthraquinone is heated at 80–110°C. with 93–96%  $\text{H}_2\text{SO}_4$  and run at 40–60°C. into water. After filtering and milling in the presence of an aq. dispersing agent the product—



can be used to produce brownish-orange spun-dyed viscose. R.K.F.

#### Fluorescent Brightening Agent

DuP

USP 2,704,296

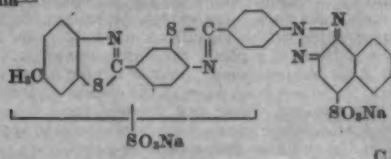
Compounds of formula—



( $\text{R} = 4''\text{-radical of Primuline or Primuline base (C.I.812)}$ ;  $\text{Q} = 1:2\text{-radical of mono- or di-sulphonaphthalene}$ ;  $\text{R}$  and  $\text{Q}$  are chosen so that the compound contains  $> 1$  sulpho group) have good affinity for cellulose to which they impart a greenish-blue fluorescence which is fast to bleaching. Thus Primuline (33.3 parts) suspended in water (1000) was diazotised at 0–5°C. using excess HCl and sodium



naphthionate (14.7) in water (430) added. The mixture was stirred for 16 hr. at room temperature. NaOH added to make it alkaline to Brilliant Yellow paper and the *o*-amino-azo dye salted out and filtered off. The wet dye cake was put in water (1600) and 28% ammonia (200) and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (50) in water (100) added. After 5 hr. refluxing, NaOH (8) in water (20) was added and the whole boiled for 1 hr. and filtered hot. The hot filtrate was agitated for 30 min. with 12% aq. sodium hypochlorite (40), treated with charcoal and filtered. The filtrate was stirred with 20% of its weight of NaCl, cooled, filtered and dried. The product was a medium brown and its aqueous solution showed bluish-green fluorescence. It is of probable formula—



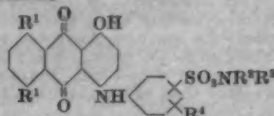
C.O.C.

#### 4-[X-Sulphamylanilino]-1:8-dihydroxy-5 (or 8)-aminoanthraquinones

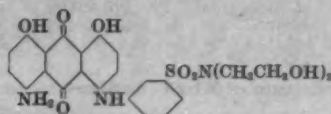
General Aniline

USP 2,704,202

Dyes of formula—



(One  $\text{R}^1 = \text{OH}$  the other  $= \text{NH}_2$ ;  $\text{R}^3 = \text{H}$ , cyanoalkyl or hydroxyalkyl (Alk of 2-3 C);  $\text{R}^4 = \text{hydroxyalkyl}$  or cyanoalkyl (Alk of 2-3 C);  $\text{R}^5 = \text{H}$  or Alk) are bright blue disperse dyes of excellent fastness to light and gas fume fading. Thus  $\text{N}^3$ [(4:6-dihydroxy-8-nitro-1-anthraquinonyl)- $\text{N}^1$ -bis(2-hydroxyethyl)metanilide (3) in water (350) was heated to  $95^\circ\text{C}$ . and  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  (5) added. The mixture was kept at  $95^\circ\text{C}$ . for 1 hr., allowed to cool to room temperature, and the dye filtered off. It dyed acetate rayon bright blue of good fastness to light and gas fume fading. It has the formula—



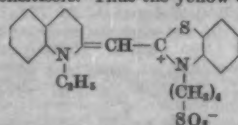
C.O.C.

#### Cyanine Derivatives—Disperse Dyes and Photographic Sensitisers

Agfa

BP 742,112

An alkane sultone is condensed with a heterocyclic N base containing an alkyl, thioalkyl,  $\beta$ -alkylthiovinyl,  $\beta$ -halogenovinyl,  $\beta$ (*N*-methylanilino)-vinyl or  $\beta$ -acyl-anilido-vinyl group and the resulting  $\omega$ -sulpho-betaine is reacted with a compound capable of converting it into a cyanine derivative. The products are disperse dyes and photographic sensitizers. Thus the yellow dye—



is made by heating 1-ethyl-2-methylmercaptoquinolinium-methyl-sulphate and 2-methyl-benzthiazolium-3-(butyl- $\omega$ -sulpho)betaine [from 3-methylbenzthiazol and butane sultone] at  $60^\circ\text{C}$ . for 1 hr. in ethanol containing triethylamine.

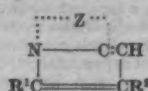
R.K.F.

#### merocyanine, Styryl and Cinnamylidene Dyes

Eastman Kodak Co.

USP 2,706,193

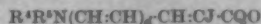
Condensing a compound of formula—



( $\text{R}^1$  and  $\text{R}^2 = \text{H}$ , Alk or Ar; Z = atoms to complete a nucleus of the pyridine or isoquinoline series), e.g. 2:3-diphenylpyrrocoline, in presence of anhydrous acid with a compound of formula—



( $\text{R}^3 = \text{Ar}$  of the benzene series;  $n = 0$  or 1), e.g. *p*-dimethylaminobenzaldehyde, yields a styryl or cinnamylidene dye. If the aldehyde is replaced by a compound of formula—



( $\text{R}^4 = \text{H}$  or acyl;  $\text{R}^5 = \text{Ar}$ ; J = cyano, carboxyl, carbalkoxyl, acyl, carbamyl or a heterocyclic quinoline nucleus; Q = OH, Alk, Ar, amino, carbalkoxyl, alkoxy and a heterocyclic benzofuran nucleus; J and Q together = atoms to complete a 5- or 6-membered heterocyclic nucleus;  $d = 0, 1$  or 2), e.g. 5-(3-acetamidodiallydene)-1:3-diethyl-2-thiobarbituric acid and condensation occurs in presence of a basic condensing agent then merocyanine dyes are formed. Both sets of products are non-migrating sensitising dyes which are readily bleached out.

C.O.C.

#### Hydrated Calcium Silicate

Columbia-Southern Chemical Corp.

BP 743,930

Concurrent streams of an aqueous calcium salt and an aqueous alkali metal silicate are merged and then turbulently agitated, the resulting calcium silicate being withdrawn in a stream from the point of agitation. The product is particularly suitable for compounding with natural or synthetic rubbers.

C.O.C.

#### Calcium Sulphate having Non-blanching Properties

National Lead Co.

BP 744,559

The blanching properties of calcium sulphate (i.e. those properties of the pigment which when used to make paint of high pigment-volume concentration cause the paint to be lighter coloured when dry than when wet) are eliminated by mixing with it 0.1-0.5% by weight of a straight chain primary amine containing  $> 7$  C, e.g. octylamine.

C.O.C.

#### Calcium-Strontium Phosphate Phosphors

Sylvania Electric Products

BP 744,063

Replacement of  $> 90\%$  of the calcium by strontium in a tricalcium phosphate activated by Sn or Sb and Mn changes the colour of the luminescence from a saturated orange red to a brighter more saturated deep red the degree of change depending on the proportion of Ca substituted by Sr.

C.O.C.

#### Carbon Black

Columbian Carbon Co.

USP 2,705,189

A method of increasing the yield when making furnace black.

USP 2,705,190

A method of producing very fine grades of furnace black.

C.O.C.

#### Converting Black Iron Oxide into Red Iron Oxide

United States Steel Corp.

USP 2,705,188

The black iron oxide is made into an aqueous slurry which is then treated with gaseous sulphur trioxide. At first there is slow evolution of heat caused by the sulphur trioxide dissolving in the water. There then follows a sudden and very marked exothermic reaction and the slurry changes into a thin mud-like mass. This is dehydrated and then roasted at  $900-1500^\circ\text{C}$ . until all the sulphur is driven off and a red pigment is left. The hue, brilliance and saturation of the pigment are controlled by varying the amount of sulphur trioxide used, and the time and temperature of roasting.

C.O.C.

Hydrogen-bond Formation. III—Reactivity of Amines, Amides, and Azo Compounds in Aqueous and Non-aqueous Solutions (VIII p. 187)

Neutrogene Dyes—Their Development and Application in Printing (IX p. 190)

Printing with *N*-Phenyl-1:4-diaminobenzene-*N'*-sulphonic Acid or its Salts (IX p. 191)

## V—PAINTS; ENAMELS; INKS

## PATENT

## Coatings containing Portland Cement and Synthetic Resin

J. Spillmann-Zupfinger and S. Pietroboni BP 743,952  
Incorporation of Portland cement, lime and a suitable colouring matter into an aqueous binder of 0.7–1.5% by wt. of methylcellulose and 7–15% of finely divided polyvinyl acetate, yields a coating composition applicable by either atomising or spraying or suitable for application in layers of any thickness on to paper, wood, fibre board, metals, plaster, etc. The resulting surface is washable and has the appearance of tapestry.

C.O.C.

## Calcium Sulphate having Non-blanching Properties (IV p. 183)

Printed Felt-base Floor Coverings (IX p. 191)

## VI—FIBRES; YARNS; FABRICS

## Second-order Transition Temperature and Fibre Properties

A. Brown

*Text. Research J.*, 25, 891–901 (Nov. 1955)

The nature of the second-order transition temperature is discussed, and associated effects, such as stiffness-temperature and resiliency-temperature variations, are considered. Experimental data are given for acetate and viscose rayon, Terylene, Orlon, dynel, Acrilan, Saran, and nylon fibres. Stiffness falls off at the second-order transition temperature and resiliency is a minimum. These effects are discussed in terms of the internal structures of the fibres, and some practical applications are considered.

W.R.M.

## Chemical Properties of Field-weathered Cotton

L. E. Hessler and D. J. Upton

*Text. Research J.*, 25, 1029–1034 (Dec. 1955)

Field weathering tests of up to 5 months' duration on early-opened cotton and up to 2 months on late-opened cotton were made under essentially dry conditions. pH values of aqueous extracts indicated that no attack by micro-organisms took place. Early-opened cotton showed an increase in cellulose content on weathering. D.P. determinations on cellulose nitrates from weathered and unweathered samples gave a measure of cellulose chain rupture. An additional D.P. determination on the weathered cotton after boiling in alkali enabled oxidative degradation to be estimated. Both forms of degradation increase with time in the field, but are less marked in late-opened cotton, owing to lower temperature and light intensity. Weathering reduced the amount of direct dye taken up by both cottons.

J.C.F.

## Molecular Properties of Milkweed Cellulose

T. E. Timell and J. L. Snyder

*Text. Research J.*, 25, 870–874 (Oct. 1955)

Seed hairs of the common milkweed are found to contain 39.6%  $\alpha$ -cellulose, 35.3% pentosan, and 15.1% lignin. Direct nitration of the fibres gave a cellulose nitrate with glucose as the only constituent sugar in a yield corresponding to a content of 29% cellulose in the original material. The average D.P. of the nitrate was 5800. The chain-length distribution had only one peak and showed right-hand skewness. The lower D.P. limit was 2500 and the upper 8000, with a maximum at a D.P. of 4000.

W.R.M.

## Stress Relaxation of Fibres as a Means of Interpreting Physical and Chemical Structure. I—Determination of Relative Accessibility

T. Lemiszka and J. C. Whitwell

*Text. Research J.*, 25, 947–955 (Nov. 1955)

Preliminary studies of stress-relaxation behaviour of synthetic and cellulose fibres in HCl and water are reported. Behaviour in water indicates that relaxation is due to scission of weaker secondary linkages. Drastic reduction of stress following addition of HCl is due to rupture of primary bonds. Stress-relaxation measurements on cellulose fibres are interpreted in terms of relative accessibility, and values obtained give the same order of accessibility as by other methods.

W.R.M.

## Applications of Thermodynamics to the Stretching of Cellulose Fibres

W. E. Roseveare and L. Poore

*Text. Research J.*, 25, 709–714 (Aug. 1955)

Mechanical deformations of cellulose are recognised as taking place primarily in the amorphous regions. Since these regions do not have a regular type of order, attention has been turned to entropy of stretching as a statistical measure of changes in structure occurring on stretching. Data are presented giving the retractive force, coefficient of thermal expansion, and elastic modulus under a wide variety of conditions. Thermodynamic treatment of the data shows that moisture content and temperature control the bonding between chains in the amorphous regions. These cross-links to a large extent determine the mechanical properties, which vary from an elastic glass in the dry state to those of a partly rubbery material in the wet state at high temperatures. At low temperatures in the wet state, the amorphous parts of the chains "precipitate" out of the swelling water and thereby form cross-links between chains, which makes the modulus tend to approach infinity at the cellulose–water eutectic point.

W.P.M.

## Heterogeneous Degradation of Cellulose. IV—Mild Hydrolytic Degradation of Cotton and Wood Pulp

T. N. Kleinert and V. Moessmer

*Text. Research J.*, 25, 778–779 (Sept. 1955)

The presence of a wetting agent accelerates only the initial degradation of a raw cotton exposed to 0.1 N-HCl at 20°C. for periods up to 350 days. During this time the dry strength decreases by almost half. Purified linters are degraded more slowly than raw cotton, and a wood pulp more slowly still.

W.R.M.

## Lignin and Hemicellulose of Jute

P. B. Sarkar and A. K. Mazumdar

*Text. Research J.*, 25, 1010–1020 (Dec. 1955)

(a) A mild alkaline pretreatment is essential for the complete removal of lignin from jute by sodium chlorite. The alkali appears to hydrolyse the chlorite-resistant ester linkage between a portion of the lignin and the polyuronide hemicellulose of the fibre. The wet strength of fibres thus treated is low compared with that of ordinary delignified jute. (b) It is found that a small proportion of lignin (ca. 0.5%) is removed from jute by treatment with dilute NaOH soln. at room temp. The properties of this alkali lignin are described. (c) An investigation of the constituents of defatted jute fibre removed by 1% NaOH at room temp. is reported.

J.C.F.

## Crease Resistance of Mixed (Amilan-Viscose Rayon) Fabrics

H. Noshi

*J. Soc. Textile Cellulose Ind. Japan*, 11, 812–816 (Dec. 1955)

The crease resistance reaches its maximum value when the proportion of viscose rayon in the fabric is 25%, but decreases after that limit. In order to evaluate the crease resistance of a fabric, measurements should be taken in all directions, as the resistance shows large differences in different directions.

AUTHOR

## Mechanism of Supercontraction in Keratin

G. M. Jeffroy, J. Sikorski, and H. J. Woods

*Text. Research J.*, 25, 714–722 (Aug. 1955)

Examination, in the electron microscope, of keratin, supercontracted by various techniques (which are described), shows that no important deformation, other than shortening, occurs in the microfibrils. The supercontraction phenomena may depend on interactions between the microfibrils and an interfibrillar matrix, each component being contractile under suitable conditions. The possibility is suggested that this matrix, located between microfibrillar sheets, has an orderly globular configuration.

W.P.M.

## Oxidation of Wool by Inorganic Per-acids

C. Earland, T. P. MacRae, G. J. Weston, and K. Statham

*Text. Research J.*, 25, 963–965 (Nov. 1955)

Permolybdic and pertungstic acids in aqueous phosphoric acid react with wool in a manner similar to peracetic acid. After oxidation, up to 90% of the wool is soluble in dilute ammonia solution, from which a protein representing 50–60% of the original wool is precipitated by addition of acid. Both the soluble protein and the insoluble residue are

found to be in the  $\alpha$ -configuration, and no material in the  $\beta$ -configuration is found, in contrast to results obtained with the peracetic-acid oxidation of wool, where material in the  $\beta$ -configuration is found in the insoluble fraction.

W.R.M.

### Wool Gelatin—Isolation of Acid Peptides from Extracts made at Room Temperature

H. Zahn and J. Meienhofer

*Text. Research J.*, 25, 739-750 (Aug. 1955)

The nature of the water-soluble protein-containing substances (wool gelatin) contained in wool has been investigated. Cleaned wool was treated with water at various temperatures. A preliminary examination showed that the room-temperature extract differed most from wool. Wool gelatins extracted by boiling wool with water became more and more similar to wool with duration of treatment. The amino acid composition of wool gelatin extracted by a 25-hr. boil was close to that of wool with the exception of the cystine contents. Further investigation of room-temperature extracts by dialysis and chromatographic analysis showed that the solution outside the membrane contained glutamic acid, aspartic acid, and some lower peptides. The inside substance contained three higher peptides which contained no basic amino acids. The amino acid composition of these peptides is given. Extracts at 50°C. and 100°C. are being examined.

W.P.M.

### Sorption of Hydrogen Chloride by Textile Fibres

P. Larose

#### II—Sorption by Modified Wool and Other Fibres

*Text. Research J.*, 25, 956-961 (Nov. 1955)

Sorption of HCl by wool is measured and compared with that by wool which has undergone different chemical treatments. Sorption of HCl by nylon, Perlon, and other synthetic fibres is also determined. Sorption-time curves are shown. The results, which confirm the view that the peptide link is mainly responsible for sorption of HCl by protein and similar fibres, are discussed with particular reference to the accessibility of reactive groups.

W.R.M.

#### III—Sorption by Proteins and by Nylon

*Ibid.*, 25, 1004-1006 (Dec. 1955)

The sorption of HCl by nylon and certain proteins is discussed in the light of recent work. Particular attention is paid to the significance of the amount of HCl retained after desorption. The changes produced in nylon on sorption of HCl are summarized. The heat of sorption is calculated, and it is concluded that there is no essential difference between the sorption of HCl by nylon and by proteins.

J.C.F.

### Angora Rabbit Fibres

S. Okajima, S. Ikeda, and H. Okamoto

#### III—Mechanical Behaviour during Cyclic Stretching and Recovery in Air and Distilled Water

*J. Soc. Textile Cellulose Ind. Japan*,

11, 750-755 (Nov. 1955)

If a wool fibre is stretched by 30% in water and released at once it recovers the original length, and the work of the second stretching after 24 hr. relaxation is equal to that of the first one; but, according to a preliminary test, this is not true for Angora rabbit hairs. So the mechanical behaviour of the latter during cyclic stretching and recovery in air and distilled water has been investigated in detail for the purpose of scientific control in the hat industry.

#### IV—Mechanical Behaviour during Cyclic Stretching and Recovery in Buffer Solutions of Various pH Values

*Ibid.*, 11, 782-787 (Dec. 1955)

The mechanical behaviour of an Angora rabbit hair in acidic buffer solutions was studied by the methods described in Part III, and the following facts were observed—

(1) When stretching and recovery are repeated after a relaxation for 5 min. after each cyclic operation, the work for 30% stretching decreases with the number of cycles.

(2) This decrement is smallest at the isoelectric point, pH 4.5, and it appears to increase as the medium becomes more acidic or more alkaline, but the magnitude of the work itself decreases at the same time, and consequently the decrement is also small and the work becomes nearly constant after 2 or 3 cycles at pH 1.1 and 1.9.

(3) The work for 30% stretching in the air is significantly smaller.

(4) The work of recovery is nearly constant and is not changed by the cycles. Its value also is a maximum at the isoelectric point, and a minimum in the air.

(5) The hysteresis is largest in the air and decreases markedly after the first stretching. In water it is also a function of pH, and the relationship is similar to that for the work of stretching.

(6) The resilience—the ratio of the work of recovery to that of stretching—is, on the contrary, larger at the lower pH value, and is a minimum in the air.

(7) The work of stretching, which is decreased by three or more cyclic operations, as described above, partly recovers when the hair is relaxed in water for 24 hr. The effect is most significant in the case of hair which has been stretched in the air.

(8) The work at 50°C. is less than that at 30°C. This temperature effect becomes larger as the pH of the medium approaches the isoelectric point of the hair.

These phenomena are explained on the basis of the folding and unfolding of the keratin molecules.

AUTHORS

### Fine Structure of Silk Fibroin. IX—Microscopic Observations and Dyeing Properties of the Fine Structure of Silk Fibroin

M. Nakanishi

*J. Soc. Textile Cellulose Ind. Japan*,

11, 788-793 (Dec. 1955)

Examination of the mechanism of dissolution of silk fibroin in dilute alkali and dilute acid solution has shown the following—(1) In the structural unit of silk fibroin, namely brin, there are a micelle unit, composed of sub-crystalline and crystalline regions, and a fibril unit of micelle unit. (2) The fibrillae run parallel to the fibre-axis, and are crowded in the interior, but at places are in disorder. Amorphous region II exists chiefly among the fibrillae, and the surface of brin is chiefly covered with amorphous region I.

AUTHOR

### Strain in Lactams

A. A. Stropikheev, S. M. Skuratov, O. N. Kashinskaya, R. S. Murotova, E. P. Brykina, and S. M. Shtekher

*Doklady Akad. Nauk S.S.S.R.*,

102, 105-108 (1 May 1955)

Determinations are made of heats of combustion at 20°C. and specific heats over the range 20-75°C. for the lactams of  $\alpha$ -aminoalkanoic acids containing 4-7 C. The heats of combustion are adjusted by calculation to the liquid state at 75°C. and are compared with the values calculated for the corresponding open-chain cpd. by the group-additivity rule (the value for  $-CH_2-$  is well established from work on hydrocarbons, and the value for  $-CO-NH-$  is calculated from measurements by the authors on *N*-butylvaleramide). In this way the component attributable to the strain present in the ring is calculated; it has the values 1.1, 2.2, 3.8, and 5.3 kcal./mole, respectively, for lactams having 4, 5, 6, and 7 C atoms. The degree of strain can be correlated with ease of polymerization—the first two lactams do not polymerize, 6-hexanolactam yields an equilibrium mixture containing 4-7% of cyclic monomer, and 7-heptanolactam is converted almost completely into linear polyamide. Similar measurements are made also for 4- and 6-methyl-6-hexanolactams, and it is concluded that substitution of methyl in 6-hexanolactam has no effect on strain, the reduced tendency for these compounds to undergo polymerization being attributable to a less favourable entropy change in the process.

A.E.S.

### Spherulitic Structure in 6,6-Nylon

R. J. Barriault and L. F. Gronholz

*J. Polymer Sci.*, 18, 393-403 (Nov. 1955)

Polarisation-microscope studies show that spherulites form readily at temperatures near the melting point. There is evidence that the spherulites form more readily on the surface than inside the polymer. X-Ray m.p. studies indicate that the true thermodynamic m.p. of 6,6-nylon must be higher than the normally accepted fusion temperature.

W.R.M.

### Photochemical Processes in Nylon at Room Temperature

R. A. Ford

*Nature*, 176, 1023-1024 (26 Nov. 1955)

When thin nylon films (ca. 20  $\mu$ . thick) are irradiated by an unscattered Hanovia 8250 U mercury are in the



presence of  $O_2$  a new absorption band develops at ca. 2900 Å. When the incident light is cut off the intensity of this band continues to increase to a higher value, initially at a greater rate. On re-irradiation, the intensity falls rapidly to a value equal to that before the dark period. These observations are taken to indicate the photolysis of the nylon into two free radicals followed by combination of one of these with  $O_2$  to produce a peroxy radical responsible for the band at 2900 Å. Simultaneously, this radical is decomposed photochemically to the original radical and  $O_2$ . It is concluded that diffusion of organic free radicals and their oxygenated products through solids is much slower than that of gaseous  $O_2$ . A.J.

#### Equilibria in Polyamide Systems from $\epsilon$ -Caprolactam and Water

P. F. van Velden, G. M. van der Want, D. Heikens, C. A. Kruissink, P. H. Hermans, and A. J. Staverman

*Rec. Trav. chim.*, 74, 1376-1394 (Nov. 1955)

The equilibrium products obtained when  $\epsilon$ -caprolactam is condensed in the presence of water at 222°C. and 254°C. in closed systems consist of unconverted caprolactam, cyclic compounds, and linear polymers. The proportion of caprolactam and cyclic compounds increases with increasing temp. and/or water content. Over the range investigated number-average D.P. of the chain fractions varied from ca. 10 to 100. The equilibrium constant of the polycondensation reaction decreases with decreasing D.P. of the products. A.J.

#### Kinetics of the Catalytic Polymerisation of $\epsilon$ -Caprolactam

E. Turska and A. Broda

*Zesz. Nauk. Politech. Lodz.*, No. 4 (Wlokiennictwo 1), 49-69 (1954)

A series of polymerisations of purified and dry  $\epsilon$ -caprolactam were performed in an atmosphere of nitrogen, in presence of caustic soda as catalyst. The caprolactam was heated to the boil, the catalyst added, and the temperature measured periodically. From the graph of temperature against time it is seen that the reaction is exothermic until a maximum is reached. The second part of the reaction is endothermic, and progresses at a much slower rate. Analysis of the samples taken periodically shows that the rise of temperature is an indication of polymerisation, which takes place until a certain concentration of the monomer is established in the mixture. Then the rate of polymerisation slows down, until it finally stops and even some depolymerisation takes place. The rate of polymerisation is greatest when 0.18% of catalyst is used—further additions retard the rate of reaction. Amounts greater than 0.5% tend to make the rate constant.

$\epsilon$ -Aminocaproic acid acts as a negative catalyst, and stops polymerisation when 0.9% of the free acid is present. The varying quantities of the free amino acid in the  $\epsilon$ -caprolactam are responsible for the unsatisfactory reproducibility of the results.

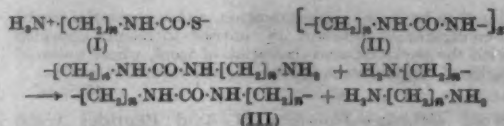
Therefore, the success of the operation depends upon the speed with which the  $\epsilon$ -caprolactam is brought to the boil. From the work done so far, the conclusion is reached that the method of thermal analysis is suitable for the investigation of the catalytic polymerisation of  $\epsilon$ -caprolactam. T.Z.W.

#### Fibre-forming Polyalkyleneureas. I—Chemical Preparation, Structure, and Mechanism of Formation

G. J. M. van der Kerk, H. G. J. Overmars, and G. M. van der Want

*Rec. Trav. chim.*, 74, 1301-1322 (Oct. 1955)

Aliphatic  $\omega$ -diamines  $NH_2[CH_2]_nNH_2$  ( $n = 6-10, 12$ ) react with carbonyl sulphide to yield thiocarbamates (I). Heating I in *vacuo* (e.g. for 6 hr. at 110°C.) causes loss of  $H_2S$ . The product contains no sulphur and is converted to a polyalkyleneurea (II) having fibre-forming properties (melt-spinning) on further heating (e.g. at 200°C.). It is considered that the first polymerisation product (non-fibre-forming) also has the structure II with lower values of  $n$ : on further heating, chain elongation occurs through aminolysis of urea groups and elimination of one molecule of monomer (III). There is good agreement in values of D.P. obtained by viscosity measurements and determination of  $-NH_2$  end-groups.



A.J.

#### Fibre Properties of Modified Aromatic Polyesters—II

W. Griehl and R. Hoffmeister

*Faserforsch. und Textiltech.*, 6, 554-562 (Dec. 1955)

Experimental details are given for preparation of modified polyesters based on polyethylene terephthalate. Melting points, second-order transition points, and the results of X-ray studies are given together with details of strength, strain, flexibility, dyeability, and other textile data. W.R.M.

#### Polyacrylonitrile Fibres (Tabulated Data)

P. A. Koch

*Textil-Rund.*, 10, 622-629 (Nov. 1955)

#### PATENTS

#### Improving the Dyeing Properties of Cellulose Esters

Hercules Powder Co. USP 2,705,689

Treating a cellulose ester having an unsaturated acyl D.S. of 0.01-1.5 with a permanganate and then removing the deposited  $MnO_2$  much increases the affinity for acid dyes. C.O.C.

#### Cellulose Thiourethans

American Viscose Corp. USP 2,705,231

Sodium xanthate in the form of either dilute viscose or coagulated into filaments is treated with an aqueous solution of a di- or trivalent metal, e.g. zinc, and then with an aqueous solution of a primary or secondary amine, e.g. aniline. Solutions so treated can be used for making filaments which, like sodium xanthate filaments so treated, have affinity for acid dyes. C.O.C.

#### Acrylonitrile Polymers of Good Affinity for Acid Dyes

Courtaulds BP 744,487

Copolymers of  $\leq 85\%$  acrylonitrile and esters of formula  $CH_2=CR^1R^2O-SO_2-R^3$

( $R^1 = H$  or  $CH_3$ ;  $R^2 =$  divalent hydrocarbon, preferably  $CH_2$ ;  $R^3 =$  subst. or unsubst. Ar) when treated with ammonia or primary, secondary or tertiary amines, yield fibre-forming polymers having good affinity for acid dyes. C.O.C.

#### Cellulose Fibre of Reduced Crystallinity (X p. 192)

Changes in the Fibre Structure of Wood Pulp during Cold Purification with Caustic Soda and Subsequent Drying (XI p. 195)

Aqueous Dispersions of Cellulosic Materials or Cellulose Derivatives and Fibres, Films, etc. produced from them (XI p. 197)

Utilisation of the Amino Acids of Silk Protein (XIII p. 197)

Depolymerisation of Polycaprolactam by Alkali-metal Carbonates (XIII p. 198)

Properties of Binary Mixed Polyamides (XIII p. 198)

Macromolecular Compounds (XIII p. 198)

Multicomponent Polyamides (XIII p. 198)

Polyacrylonitrile Fibres (XIII p. 198)

#### VII—DESIZING; SCOURING; CARBONISING; BLEACHING

#### Visual Observation of the Behaviour of Soil Particles in Dilute Aqueous Soap Solutions

C. W. Hoek

*Text. Research J.*, 25, 682-685 (Aug. 1955)

An electron-microscopical study of the effect of the addition of graphite to soap solutions of laundry strength is discussed with illustrations of the electron-micrographs obtained. The method of preparation of the specimens is described. The soap particles, which may bear some relation to micelles, measured 100-150 Å. wide and 500-1500 Å. long. The graphite became coated with elongated soap particles, which were distributed unevenly owing to their aggregation round the graphite particles. The soap particles, when no graphite was present, were distributed evenly throughout the solution. W.P.M.



**Solvent Scouring of Grease Wool. I—Review**

D. P. Norman and W. W. A. Johnson

*Amer. Dyestuff Rep.*, 44, 893-900, 911 (19 Dec. 1955)

The principles and the practice of the solvent scouring of wool are thoroughly reviewed. The theory of liquid-solid extraction is discussed both generally and in relation to wool, with flow charts. Factors governing choice of solvent are listed, and a description is given of percolator, counter-current, multiple-contact, and continuous-extraction systems. Methods of separating solids from the miscella (solvent extract), the recovery of extracted materials, and solvent recovery are more briefly discussed. A detailed description is given of the requirements and methods used for wool in particular.

J.W.B.

**Polarographic Behaviour of the Chlorite Ion**

N. Konopik and E. Werner

*Mh. Chem.*, 86, 937-951 (Dec. 1955)

## PATENTS

**Bleaching Wool with Simultaneous Reduction in Felting Power**

Institut Textile de France and Centre de Recherches Textiles

BP 743,927

The wool is treated with a cold acid solution of a chlorite until the fibres are pink and then it is bleached with a reducing solution. Thus wool fabric is impregnated with its own weight of a cold 2% aq. soln. of sodium chlorite buffered to pH 3.5 and containing 0.05% of a wetting agent. It is left exposed to air for 1 hr., rinsed, treated for 30 min. at 50°C. in an aqueous solution containing 1.5% NaHSO<sub>2</sub>, 35% Be., 0.5% conc. sodium hydrosulphite and 0.05% wetting agent, rinsed and dried. A white, shrink-resisting wool is obtained.

C.O.C.

**Desizing Glass Fibres and Fabrics**

Fothergill &amp; Harvey

BP 744,424

The carbonaceous constituents of the size are removed by aqueous or other solutions of soap or other detergent, the yarn or fabric is then dried and heated for a brief period, e.g. 5 min., to 200-290°C., to remove the residual size.

C.O.C.

**Combined Cleansing and Sizing of Carpets and Pile Fabrics**

(X p. 194)

## VIII—DYEING

**Historical Notes on the Wet-processing Industry. X—Yankee Dyers**

S. M. Edelstein

*Amer. Dyestuff Rep.*, 44, 887-891 (5 Dec. 1955)**Rate of Dyeing**

J. H. Skinkle

*Text. Research J.*, 25, 861-865 (Oct. 1955)

The influence of diffusion on the rate of dyeing is discussed. The effects of different reactivity and accessibility of fibres are considered. These lead to a sigmoid rather than a linear plot of fractional dye exhaustion against square root of time of dyeing. It seems that assumptions used in the simplification—

$$\frac{E}{E_{\infty}} = 2\left(\frac{Dt}{\pi}\right)^{1/2}$$

( $E$  = exhaustion,  $D$  = diffusion coefficient) are incorrect and that the linear part of the plot is related only by chance to that period of dyeing  $t$  considered as corresponding to diffusion.

W.R.M.

**Hydrogen-bond Formation. III—Reactivity of Amines, Amides, and Azo Compounds in Aqueous and Non-aqueous Solutions**

F. M. Arshid, C. H. Giles, S. K. Jain, and A. S. A. Haasen

*J.C.S.*, 72-75 (Jan. 1956)

Refractometry and dielectric-constant measurement are applied to the detection of complex formation in binary systems containing basic and other nitrogenous compounds in aqueous and non-aqueous (acetone, aniline, benzene, CCl<sub>4</sub>, dioxan, diethyl ether, ethanol, and toluene) solutions. One of the aims is the elucidation of the mechanism by which certain polymers, especially proteins, adsorb organic solutes, including dyes, and, for this purpose, various amide and amino opd. have been used as models of these polymers. The reactions of certain simple aliphatic amides

with a variety of second solutes are tentatively interpreted as indicating that the enol tautomer of the unsubstituted or N-monosubstituted compounds predominates in most non-aq. soln. and the keto form in aq. soln. The free N atom in sulphonated o-hydroxyazo opd. forms complexes with phenol in aq. soln., but not, apparently, with alcohols. Diethylamine appears to react by salt formation with the sulphonic acid groups. Trichloroethylene in organic solvents forms a complex by a C-H...N bond with the azo group, which may explain its good solvent power for unsulphonated azo dyes. The presence of a chelate ring in aniline-2-naphthylamine is revealed by its complex ratio with phenol compared with those of aniline-1-naphthylamine and phenol.

H.H.H.

**Theoretical Bases of High-temperature Dyeing**

M. Domingo Ferré

*Ingeniería Textil*, 22, 503-516 (Nov.-Dec. 1955)

The subject is briefly reviewed historically, and the influence of temperature on factors in the dyeing processes, e.g. distribution of dye and exhaustion, considered. The processes available are—(a) dyeing in non-aqueous media of high b.p., (b) dyeing in conc. aq. soln., (c) pigment-padding and steaming, and (d) dyeing in closed static or dynamic high-pressure systems. Direct, acid, vat, metal-complex (lower and higher pH types), chrome, Sandocryl (8), and disperse dyes are reviewed, with a discussion of the high-temperature dyeing of cotton, viscose and acetate rayons, nylon, Orion, Daeron, and wool.

S.R.C.

**Pad-Roll Dyeing System and its Application**

C. O. Eriksson, N. Landqvist, and B. Mellbin

*Amer. Dyestuff Rep.*, 44, P 877-P 881 (5 Dec. 1955)

A detailed description of this Swedish process is given.

J.W.B.

**Equilibrium Dyeing of Cotton with Direct Dyes**

P. V. Morfoganov and B. N. Mel'nikov

*Tekstil. prom.*, 15, 33-36 (Aug. 1955)

Equilibrium dyeing and desorption experiments are carried out on cotton with Chrysophenine (I), Direct Blue (II) [identity uncertain], Direct Violet (III) [probably C.I. 394], and Direct Diazo Black (IV) [probably p-nitroaniline-2-methoxy-5-methylaniline-γ acid (alkaline coupling), and reduce nitro group]. The standard affinities ( $-\Delta\mu^\circ$  in kcal./mole) of the dyes at 25, 60, 70, 80, 90, and 100°C. are found to be, respectively—I: 5.22, 4.28, 4.04, 3.78, 3.52, 3.26; II: 6.25, 5.15, 4.80, 4.45, 4.10, 3.73; III: —, 5.50, 5.35, 5.20, 5.05, 4.90; IV: —, 6.56, 6.24, 6.06, 5.75, 5.40. The standard heats of dyeing ( $-\Delta H^\circ$  in kcal. per mole) are found to be—I: 12.9; II: 16.5; III: 10.5; IV: 16.5.

A.E.S.

**Continuous Dyeing of Cotton Piece Goods with particular reference to Vat and Soluble-vat Dyes**

M. R. Fox

*Amer. Dyestuff Rep.*, 45, P 39-P 40 (16 Jan. 1956)

Factors which may give trouble in continuous vat dyeing of cotton piece goods include—(1) thermal effects, in which the false belief that temperatures up to 200°F. cause superior penetration leads to faults because they more probably induce aggregation; (2) storage time of the padding liquor, which should be  $> 2\frac{1}{2}$  hr.; (3) vigorous agitation, which can cause collapse of the dispersion; (4) unsuitable dispersing agents (Calsolex Oil H8 is the best), which anyway can be dispensed with at temp.  $> 140^\circ\text{F.}$ , and which cause aggregation; and (5) the effects of electrolyte and foreign matters. Hydrosulphite decomposition and ideal concentrations are discussed, and a list of suitable solubilised vat dyes is given together with general remarks on application.

J.W.B.

**Use of the PKM Hank-dyeing Machine for Dyeing with Vat Dyes**

I. D. Zakhar'evskaya, L. I. Onikov, and N. F. Markov

*Tekstil. prom.*, 15, 20-31 (June 1955)

The PKM hank-dyeing machine is a rotating-arm machine in which the arm carrying the hanks is a perforated cylinder through which a regulable amount of the dye liquor is circulated so that it passes through the hanks as they rotate. It is found that this machine can be used satisfactorily for vat dyeing, the main precaution necessary being an increase in the amount of hydrosulphite added (to combat increased oxidation by air).

A.E.S.

### Application of Soledon Dyes to Spun Viscose Rayon Staple Piece Goods

J. B. Jackson

*Dyer*, 114, 907-910 (9 Dec.), 985-993 (23 Dec. 1955)

A fairly comprehensive survey which deals with the chemistry of Soledon dyes, their dyeing properties and dyeing methods, the use of dyeing assistants, and application to fabric-fibre blends of viscose-acetate rayon, viscose rayon-nylon, and viscose rayon-cotton. Optimum application conditions of temperature,  $\text{NaNO}_2$ , and  $\text{H}_2\text{SO}_4$  concn., etc. are given in table form for each member of the range.

A.H.

### Direct Dyeing of Cellulose. III—Dyeing Properties of Congo Red and Benzopurpurin 4BKX Conc.

K. Nishida and I. Sugiyama

*J. Soc. Textile Cellulose Ind. Japan*, 11, 744-749 (Nov. 1955)

The absorption isotherms of Congo Red (C.I. 370) and Benzopurpurin 4BKX conc. (C.I. 448) at 90°C. from baths containing  $0.05 \times 10^{-3}$ ,  $0.1 \times 10^{-3}$ , and  $1.0 \times 10^{-3}$  mole of dye with varying salt concentration of 0.05-3.0 mole of  $\text{NaCl}$  per kg. of dye liquor were determined using the photoelectric colorimeter, and the relations between the chemical constitution of dyes, the aggregating properties of dye anions, and the affinity for cotton were studied. The presence of a  $\text{CH}_3$  group in the dye molecule increases the affinity of the dye for cotton, but an  $\text{SO}_3\text{Na}$  group decreases the affinity. The aggregating tendency of the dye in solution increases with increasing affinity of the dye. The effects of salting out by the electrolyte upon the dyeing properties are found to be important.

AUTHORS

### Dyeing of Cellulosic Fibres at Temperatures above 100°C.

J. Vila Baqués

*Ingeniería Textil*, 22, 517-534 (Nov.-Dec. 1955)

The advantages and the disadvantages are discussed together with the factors affecting the chemical stability of the dyes and fibres and levelling. A, B, and C classes of direct dye with the best approach in each case are considered, noting especially the dyeing of viscose rayon cakes. The influence of temperature on rate, migration, and affinity in vat dyeing is studied, and the problem of the stabilisation of the leuco compound discussed. Cotton dyeing and viscose rayon dyeing at high temperatures are finally reviewed.

S.R.C.

### Rayon in Tufted Carpeting

L. L. Walmsley, W. S. Sollenberger, and D. P. Feyler

*Amer. Dyestuff Rep.*, 45, P 30-P 33 (16 Jan. 1956)

Rayon tufted carpets are being increasingly manufactured, and problems associated with dye selection and piece dyeing are discussed, with particular reference to warp streaks and similar faults, and to discoloration and water spotting. Blending with nylon and acetate rayon may lead to trouble through unsuitable tinting dyes, and attempts to cover the nylon with direct dyes may also lead to streakiness. Overdrying, particularly in the alkaline condition, is dangerous, and much discoloration trouble can be avoided by an acid rinse. Snags arising from the use of soil-resist treatments are also considered, and some simple test methods for tint and dye selection are described.

J.W.B.

### Dyeing with Acid Dyes

F. I. Sadov and I. A. Shilanova

*Kolloid. zhur.*, 17, 124-130 (1955)

*Chem. Abs.*, 49, 9932 (25 July 1955)

The uptakes of highly purified acid dyes are determined at various concentrations (i.e. also various pH values) for wool, silk, and 6-nylon, and affinities  $\Delta\mu$  are calculated. In agreement with theory,  $\Delta\mu$  is independent of dye concn. At given pH, the uptakes of monosulphonic acids are greater than those of disulphonic acids. The amounts of dye absorbed are much greater than can be accounted for by the amino groups of the fibres.

A.E.S.

### Chromed Wool

H. F. Bichsel

*Textil-Rund.*, 10, 471-479 (Sept.),

541-551 (Oct.), 603-611 (Nov. 1955)

A study of the uptake of chromic acid as a function of  $\text{H}_2\text{SO}_4$  concn. (0-3.5% on wt. of wool) and  $\text{K}_2\text{Cr}_2\text{O}_7$  concn. (0.5-3.0%) showed that the amount of chromic acid taken up at first increased rapidly with increasing acid concn.,

finally tending to a constant value for a given initial concn. of  $\text{K}_2\text{Cr}_2\text{O}_7$ . Chroming was carried out at room temp. Chromed samples had a somewhat reduced cystine content (up to 10% decrease), and a linear relation was found between reduced Cr and cystine content. Two-dimensional paper chromatograms of hydrolysates of chromed wool showed a weak spot due to cystic acid, but otherwise no qualitative differences from control samples. On extraction of chromed wool with 0.04 M  $\text{H}_2\text{SO}_4$  at the boil or with 0.5 N ammonium oxalate (pH 8) at 50°C., the Cr content at first fell rapidly, eventually reaching a constant value of ca. 0.1% on the wt. of the fibre. This amount of firmly bound Cr ("active Cr") was found to correspond to minimum supercontraction. The active Cr is largely responsible for the reduced regain of chromed wool, owing to the blocking of hydrophilic groups by the formation of new cross-linkages. The breaking strength of single fibres is not altered by chroming, but the elongation at break is much reduced. This is also attributable to the formation of new cross-linkages. The felting tendency of yarns was shown to be much reduced by chroming. The increased resistance of chromed wool to attack by bacteria and the larvae of clothes moths and dermestid beetles was demonstrated.

J.C.F.

### Dyeing of Wool and Mixtures containing Wool at Temperature above 100°C.

J. Vila Baqués

*Ingeniería Textil*, 22, 554-566 (Nov.-Dec. 1955)

The major limitation is the lack of resistance of the wool fibre. Dyes sensitive to prolonged boiling under normal conditions must be excluded. To reduce fibre attack and maintain winding properties, the pH of the dyebath must be in the range 3.3-6.5, preferably at the isoelectric point. The best temperature is 105-106°C. (in no case exceeding 108°C.), and the time in the preferred pH range must not exceed 20 min. Migration at 110°C. is three times that at 95°C. Recommended methods for dyeing low-pH metal-complex dyes, levelling and neutral-dyeing acid dyes, Xylene Fast P (8) dyes, Lanacyl (8), metachrome, and afterchrome dyes are discussed, and a preliminary report is made of experimental work on dyeing wool in admixture with Viscosilla, Cuprama, nylon, or Merinova.

S.R.C.

### Effect of Buffer and Electrolyte on the Diffusion of Acid Dye in Gelatin

R. B. Pontius, M. L. Kaplan, and R. M. Husney

*J. Physical Chem.*, 60, 9-12 (Jan. 1956)

A freeze-drying technique is described for measuring diffusion of dyes in gelatin on a microscopic scale. The effects of additions of buffer and electrolyte to the dyebath are studied. The maximum concentration of dye in the gelatin is apparently not reached at the gelatin surface at the start of dyeing. Difficulties in computation of diffusion coefficients are discussed.

W.R.M.

### Dyeing of Acetate Rayon with Disperse Dyes. V—Diffusion Coefficients in Cellulose Acetate Film

C. L. Bird, F. Manchester, and D. F. Scott

*J.S.D.C.*, 72, 49-55 (Feb. 1956)

Values for diffusion coefficients, ranging from  $0.05$  to  $4.8 \times 10^{-10}$  cm.<sup>2</sup>/sec., have been determined at 80°C. for disperse dyes in cellulose acetate film. The results indicate that the rate of dyeing of disperse dyes is mainly governed by the rate of diffusion in the fibre.

AUTHORS

### Dyeing of Cellulose Acetate with Non-ionic Dyes. III—Dyeing from the Vapour Phase

T. G. Majury

*J.S.D.C.*, 72, 41-49 (Feb. 1956)

A study has been made of the absorption from the vapour phase, by secondary cellulose acetate, of five model dyes. These are *p*-nitroaniline, *NN'*-dimethyl-*p*-nitroaniline, azobenzene, *p*-aminoazobenzene, and *NN'*-dimethyl-*p*-aminoazobenzene. The amounts absorbed at equilibrium have been measured, and their dependence on the vapour pressure of the dyes and the temperature of the substrate has been established.

The vapour pressures of the dyes have been measured over a range of temperatures, those of azobenzene by manometry and the remainder by Knudsen's effusion method. The results together with the absorption data yield absorption isotherms from which are derived the isosteric heats of absorption of the dyes on cellulose acetate.

The values, in the above order, are as follows—21.2, -21.4, -17.8, -22.0, and -22.7 kcal./mole.

The vapour pressure data are also used to evaluate the heats of vaporisation or sublimation of the dyes. These heats are applied to aqueous dyeing data already published to derive the absolute heats of association of the dyes on cellulose acetate. The results are in substantial agreement with the heats of absorption of the vaporised dyes.

A brief study has been made of the absorption by nylon and Terylene of vaporised azobenzene. The results for nylon yield a value for the heat of absorption of -18.0 kcal./mole. The results for Terylene are insufficiently complete for quantitative treatment. **AUTHOR**

### Cibacetyl Dyes on Synthetic Fibres

B. Kramrisch

*Dyer*, 114, 947-951 (9 Dec. 1955)

A report on the use of Cibacetyl dyes for dyeing nylon, Terylene, Orlon, and triacetate rayon. A comparison is made with the colouring of these fibres by other means, viz. acid dyes (cuprous ion method), direct dyes, and azoic dyes (modified process). **A.H.**

### Advances in Dyeing and Finishing Man-made Fibres

P. L. Meunier

*Amer. Dyestuff Rep.*, 45, P 8-P 11 (2 Jan. 1956)

Recent advances, in dyeing mainly, in the processing of Orlon, Acrilan, Dacron, nylon, and cellulose triacetate fabrics are discussed. **J.W.B.**

### Dyeing of Man-made Fibres at High Temperature

M. Domingo Ferré

*Ingeniería Textil*, 22, 535-553 (Nov.-Dec. 1955)

A temperature of 120°C. represents the limit, since nylon, Orlon, Terylene, and Dacron undergo a shrinkage of 8-10% thereat, causing channelling, etc.  $\text{CH}_3\text{COOH}$  and  $\text{H-COOH}$  are safe at this temperature, but  $\text{H}_2\text{SO}_4$ ,  $\text{Na}_2\text{PO}_4$ , soaps, and some detergents have a degrading action, which must be compensated for by a very brief exposure. Direct dyes are generally more stable on nylon than on cellulose at high temperatures. High-temperature dyeing of nylon gives poorer covering of chemical irregularities; fastness, saturation limit of direct, acid, and Lanaset (S) dyes, covering power of disperse dyes, and the practical levelling of dyes are unchanged; whilst penetration, ease of chroming, covering power of acid dyes, and colour yield of disperse dyes are improved. The dyeing of Orlon with disperse, Sandocryl (S), vat, and basic dyes and of polyester fibres with disperse and vat dyes are discussed in some detail. **S.R.C.**

### Diffusion of Disperse Dyes in Nylon Yarn

C. L. Bird and D. F. Scott

*J.S.D.C.*, 72, 56-57 (Feb. 1956)

Diffusion coefficients and times of half-dyeing have been determined for three commercial anthraquinoid disperse dyes on nylon yarn. The results support the view that rate of dyeing is mainly governed by rate of diffusion of dye in the fibre. **AUTHORS**

### Dyeing of Nylon with Acid Dyes. I—Measurement of Affinity and the Mechanism of Dyeing

E. Atherton, D. A. Downey, and R. H. Peters

*Text. Research J.*, 25, 977-993 (Dec. 1955)

It is shown that at low dye concn. dye is adsorbed on amino groups, and saturation values under these conditions agree with the number of amino groups present in the fibre. For polysulphonated dyes of low affinity this saturation value may be reduced because of the difficulty of accommodating the sulphonyl groups in the fibre. At higher dye concn. or lower pH values the fibre can take up excess dye as the undissociated dye acid. The extent of over-dyeing is greater, the smaller the number of sulphonyl groups in the dye molecule and the greater its affinity. A more generally applicable equation relating desorption data and affinity is deduced by statistical thermodynamic considerations based on the requirements of stoichiometry. The affinities for nylon of twelve acid dyes have been determined by desorption with inorganic anions, fibre saturations being kept at 50% or less of the amine titre. The effect on affinity of structural variations within a related series of dyes is examined, and the results are shown to be in agreement with data for acid dyes on wool. **J.C.F.**

### Sandocryl Process for Dyeing Polyacrylonitrile Fibres

C. H. A. Schmitt, C. W. Saalfrank, and H. R. Walker

*Amer. Dyestuff Rep.*, 44, P 904-P 907 (19 Dec. 1955)

If copper sheet, mesh, or powder is introduced into a dyebath containing copper sulphate the equilibrium  $\text{Cu} + \text{Cu}^{2+} \rightleftharpoons 2\text{Cu}^+$  is established, the balance being well to the left. If polyacrylonitrile is present, the  $\text{Cu}^+$  is adsorbed, a continuous fresh supply is automatically made available, and the possibility of Cu precipitation or dye degradation is avoided. Means of introducing the copper as sheet or mesh in different types of machine are discussed, e.g. 30 sq. in. of plate per gal.(U.S.A.) of dye liquor or a total of 60 sq. in. surface area per gal.;  $\frac{1}{8}$  oz. of 30-gauge mesh per gal.(U.S.A.), or 1-1.5% Cu powder on wt. of fabric. Effects of varying dyeing conditions, Cu surface,  $\text{CuSO}_4$  concentration, time, temperature, and pH are fully discussed, and although it is admitted that certain precautions are necessary, it is considered that they are outweighed by the consequent easy dyeing of Orlon Type 42. **J.W.B.**

### Dyeing of Acrilan

W. H. Hindle

*Amer. Dyestuff Rep.*, 45, P 34-P 37 (16 Jan. 1956)

Acrilan can be dyed with eight classes of dyes, and methods of applying disperse, metal-complex, acid, chrome, vat, soluble-vat, and direct dyes to 100% Acrilan are described. Particular attention is paid to Acrilan-wool blends, Acrilan-rayon blends being discussed more briefly. A useful bleach is obtained with acidified sodium chlorite; the material is pretreated with sulphuric acid (2 g./litre) for 20 min. at 200°F., any danger of metal stains being eliminated by incorporating phosphoric acid in this pretreatment and also in the rinse after the bleach. **J.W.B.**

### PATENTS

#### Dyeing in a Molten-metal Dyeing Machine

Standfast Dyers & Printers

BP 744,461

Modification of BP 620,584 (*J.S.D.C.*, 65, 412 (Aug. 1949)). Sludge formation by the action of the liquors floating on the molten metal can be avoided by replenishing the liquors at the same rate as they are absorbed by the fabric, the replenishing liquor being heated immediately before it enters the bath. **C.O.C.**

#### Dyeing Wool, Silk, and other Protein Fibres

R. Matalon

BP 744,042

Scouring the material in an aqueous liquor containing organic and/or inorganic acids and a wetting agent, there being the equivalent of  $\frac{1}{2}$  0.7%  $\text{H}_2\text{SO}_4$  present, gives thorough cleansing and the material can go straight into the dyebath without being rinsed. Wool so cleansed is quickly and evenly dyed. Thus wool (10 parts by wt.) is worked for 15 min. in a liquor containing water (200),  $\text{H}_2\text{SO}_4$  (1) and 10% aq. sodium lauryl sulphate (5). It is then taken out and placed in a dyebath containing Neolan Red GR. The resultant dyeing is much brighter than that obtained on alkaline-scoured wool. **C.O.C.**

#### Improving the Dyeing Properties of Cellulose Esters (VI p. 186)

#### Padding and Printing of Vat Dyes—Hydrosulphite Development Process (IX p. 190)

#### One-bath Development of Esters of Leuco Vat Dyes by the Chloramine Method (IX p. 190)

#### Coloured and Embossed Effects on Synthetic Thermoplastic Materials (X p. 194)

#### Patterned Mechanical Finish on Thermoplastic Sheets or Fabrics (X p. 194)

### IX—PRINTING

#### Modern Printing Processes

E. C. A. Wolff

*Textil-Rund.*, 10, 533-540 (Oct. 1955)

A discussion of modern printing methods with special reference to the printing of cotton, rayons, and man-made fibres. **J.C.F.**



### Neutrogene Dyes— Their Development and Application in Printing

H. Schulzen

*Z. ges. Textilind.*, 58, 30-34 (5 Jan. 1956)

The development of various types of stabilised mixtures of naphthols and diazonium salts, together with the stabilisers used, is described. Neutrogene (Fran) dyes contain a selected stabilised amine which permits development of prints in neutral steam. The application of Neutrogenes in machine and screen printing is detailed.

B.K.

### Printing with Diphenyl Black

N. E. Fedorova and I. B. Migacheva

*Tekstil. prom.*, 15, 30-32 (March 1955)

By the use of Leucotrope O (benzylidimethylphenylammonium chloride) in Diphenyl Black printing pastes, full blacks can be obtained on cotton with less tendering than that produced when various recipes recommended in the literature are used. The printing paste, which is thickened with starch, contains (per litre)—60 g. of 4-aminodiphenylamine hydrochloride, 40 g. of ethylene glycol or glycerol, 120 g. of 30% acetic acid, 50 g. of potassium chlorate, and 80 g. of Leucotrope O. The Leucotrope O decomposes with liberation of acid during steaming.

A.E.S.

### Padding and Printing of Vat Dyes— Hydrosulphite Development Process

G. Bernardy and W. Küppers

*Textil-Praxis*, 11, 63-71 (Jan. 1956)

Various processes for the application of vat dyes by padding and printing are detailed. Special attention is given to the hydrosulphite development process, which consists of four stages—(1) impregnation of the material with the padding liquor, (2) penetration, (3) conversion of the vat dye to its leuco state, and (4) fixation by diffusion of the leuco vat dye from the thickening into the fibre.

B.K.

### One-bath Development of Esters of Leuco Vat Dyes by the Chloramine Method

V. E. Rostovtsev

*Tekstil. prom.*, 15, 37-38 (Aug. 1955)

The author has previously described a two-bath method of developing Kubozols (sulphuric esters of leuco vat dyes) on cellulose fibres in which the fabric, prepared in Chloramine T, is printed with a thickened acetic acid soln. of the Kubozol and dried to effect development, or is padded with an acid soln. of the Kubozol and steamed (*ibid.*, 14, 34-36 (April 1954)). He now shows that pure fabric may be printed with a thickened alkaline soln. (the amount and kind of alkali vary from one Kubozol to another) containing both Chloramine T (40-70 g./litre) and Kubozol, dried, and passed for a few sec. through a hot acid bath (generally 10-20 g. of acetic acid per litre). Analogous methods can be used in pad dyeing. Some Kubozols can be printed on naphtholated fabric and developed by steaming (an increased concn. of Chloramine T is required), and such prints resist the subsequent coupling of a diazo compound.

A.E.S.

### Decomposition of Sodium Formaldehyde-sulphoxylate (Formosul)

W. F. Liquori

*Dyer*, 114, 827-828 (25 Nov. 1955)

A study has been made of variables which can bring about decomposition of Formosul at various stages in the printing process. For example, some vat dyes exert a greater catalytic decomposing action than others; also anthraquinone and iron salt additions to the print paste increase the loss of Formosul. During air exposure loss is more rapid in presence of starch tragacanth thickening than with British gum, this effect being reversed, however, by steaming. Exposure to air between printing and steaming can cause severe loss if humidity conditions are not suitable; e.g. dry  $\text{Na}_2\text{CO}_3$  induces better stability at this stage than  $\text{K}_2\text{CO}_3$ , owing to the critical R.H. being raised by its use from 45% to approx. 60%. The temperature of drying the print is important in maintaining stability of Formosul, since, although 95% remains after drying at approx. 100°C., only 20% is left when dried at 150°C. Initial concentration is important if effective quantity is to remain available for dye reduction during steaming.

A.H.

### Thiourea Dioxide (Manofast) in Textile Printing

P. Krug

*Dyer*, 114, 939-947 (9 Dec. 1955)

A review of the uses of thiourea dioxide as an acidic reducing agent. Application of vat dyes to acetate rayon, polyamide fibres, polyester fibres, wool, silk, and mixtures of some of the above are summarised.

A.H.

### Improvement of Discharge Whites on Para Brown Dyeings

A. G. Emel'yanov

*Tekstil. prom.*, 15, 43-45 (Oct. 1955)

Improved discharge whites on Para Brown dyeings are obtained—(a) by use of a large excess of diazo component for the coupling (in the process described, both the original dye and the diazo component are applied by padding, development being carried out in steam); (b) by thorough washing with hot dil. acetic acid after development; (c) by addition of sodium "hexametaphosphate" (50 g./kg.) and ammonium salts to the formaldehyde-sulphoxylate discharge paste; and (d) by washing the steamed goods in dil. acetic acid at 50°C. before giving the usual rinsing and soaping treatments.

A.E.S.

### Coloured Discharge Printing

G. Bertolina, A. Broggi, and A. Scarpella

*Dyer*, 114, 775-779 (11 Nov. 1955)

Economic and technical difficulties which have hitherto been associated with the discharge printing of acetate rayon, acetate-viscose rayon, and nylon fabrics are discussed, and recent patents using thiourea dioxide as the reducing agent with vat-dye printing pastes are mentioned. The restricted use of vat dyes for polyamide fibres on account of inferior light fastness, however, has led to the introduction of pigments (Aridye) with zinc formaldehyde-sulphoxylate as the reducing agent thickened with Aridye Clear 6150. In view of lack of brightness and possible impairment of fabric handle with pigments, a new discharge technique using selected direct and disperse dyes as discharge colours and thiourea dioxide as discharging agent is described. A list is given of dyes suitable for use as illuminating colours, and it is pointed out that, since the dyed grounds are either direct or disperse dyes, these are quite suitable on fastness considerations. The particular suitability of Astrazon dyes for viscose-acetate rayon mixtures is pointed out, as is also the freedom from halo effects when thiourea dioxide is used.

A.H.

### Printing of Nylon

R. E. Fletcher

*Dyer*, 114, 770-781 (11 Nov. 1955)

The advantages and limitations of various dye classes (vat, disperse, Neolan, Cibalan, direct, acid, Orama pigment) are discussed. The acid and direct ranges include dyes which are considered to give the best brightness and fastness properties. Printing is facilitated by addition of assistants—(a) acids (hydroxyacetic, acetic, lactic, and tartaric) and (b) acid-forming compounds ( $\text{NH}_4$  oxalate and  $\text{NH}_4$  tartrate), which precipitate and fix the dye during steaming; (c) solvents and swelling agents (urea, Cellosolve), to ensure penetration and dispersion of dye in the printing paste. The effect on the strength of nylon of various dispersing and swelling agents has been studied, and fluidities are compared with the fluidity of untreated nylon.

A.H.

### Printing of Polyacrylonitrile Fibres by the Sandocryl Process

E. Metzger

*Textil. prom.*, 21, 13-15 (Jan. 1956)

The anthraquinonoid acid Sandocryl (8) dyes may be printed by incorporation of a cuprous oxide preparation (copper-Sandox) and an acid-generating salt in the paste, followed by drying and cottage-steaming, e.g. for 15 min. at 0.5 atmosphere.

S.R.C.

### Lithographic Prints on Fabrics

E. Treplka

*Zest. Nauk. Politech. Lodz.*No. 6 (*Chemia* 2), 53-58 (1955)

Various methods of printing on textile fabrics are discussed. The advantages of lithographic printing, if it could be applied to textiles, are enumerated. The line of approach in intended research on the problem is outlined.

T.Z.W.



**Screen Printing**

Zimmer's Erben

BP 743,850

A roller of small diameter can be used as the squeegee even with very wide screens if it is prevented from bending by being supported by one or more rollers of greater diameter than itself.

C.O.C.

**Screen Printing**

Kerag Kessel Schmiede Apparate- und Maschinenbau

BP 742,961

The fabric is led around a rotatably supported cylinder constant tension being maintained in it during the whole printing process by a system of guide rollers and tensioning rods. In the shifting of the repeat on the curved surface of the cylinder the fabric is so fixed by friction that it cannot be displaced. Printing takes place so that a flat screen on the curved surface of the cylinder to which it can be coupled, positively rolls off by displacement in a tangential plane and co-operates with a stationary wiper effective on the cylinder in the generating line of this tangential plane. As the fabric has not to be stuck to the cylinder any type of dye can be used. In addition much more accurate and sharper prints are obtained as the screen only lies on the base on the line of contact so that the printing paste separates evenly without spurring from the meshes of the gauze whereas in previous processes the screen is lifted off as a whole after the printing over of all the surface it covers.

C.O.C.

**Preventing Indigoid Vat Dye Printing Pastes from Attacking Copper**

Allied Chemical &amp; Dye Corp.

USP 2,705,668

The tendency of printing pastes containing indigoid vat dyes to tarnish copper is inhibited by incorporating into the paste a copper chelate of a polycarboxyamine containing  $>1$  carboxymethyl radical directly linked to a basic N atom, e.g. the copper chelate of ethylenediaminetetraacetic acid.

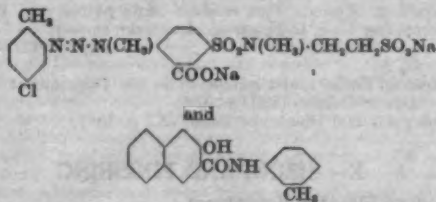
C.O.C.

**Azoic Printing Pastes**

FBy

BP 743,308

Addition of halogeno fatty acids to the printing paste and using 1-2 mol. only of fixed alkali per mol. of coupling component results in considerable increase in colour value, marked improvement in the keeping quality of the paste and to approximately the same depth of print on artificial fibres as on cotton. Thus 60 g. of an equimolecular mixture of—



are pasted with glycolmonoethyl ether (60 g.) and after adding 38% B6. NaOH (8 g.) dissolved in warm water (252 g.). The whole is then stirred into neutral starch-tragacanth thickener (500 g.) and after adding Na monochochloroacetate (30) water (100 g.) added. This yields clear deep red prints of equal strength on both cotton and spun viscose fabrics.

C.O.C.

**Printing with N-Phenyl-1:4-diaminobenzene-N'-sulphonic Acid or its Salts**

Fran

BP 744,939

Free N-phenyl-1:4-diaminobenzene-N'-sulphonic acid is obtained by treating a solution of its sodium salt with an acid. The free acid is stable and is readily separated free from mineral salts because of its low solubility in water.

Its salts with Group II metals and with nitrogen bases of formula  $NR^1R^2R^3$  ( $R^1, R^2$  and  $R^3 = H, \text{Alk}, \text{hydroxyalkyl}, \text{alkoxyalkyl}$  or aminoalkyl;  $R^1$  and  $R^2$  may together form part of a heterocyclic ring) are much more soluble than the Na salt and so are more suitable for use in printing pastes.

Thus cotton or viscose rayon is printed with N-phenyl-1:4-diaminobenzene-N'-sulphonic acid (67 g.), 20% ammonia (45), 12%  $NH_4ClO_4$  (290), 1%  $NH_4$  vanadate (20),

water and thickener (576), dried, steamed for 10 min., washed for 20 min. in boiling water containing 2 g. soap and 2 g.  $Na_2CO_3$  per litre. Intense black prints are obtained.

BP 744,940

Printing pastes containing large proportions of Na N-phenyl-1:4-diaminobenzene-N'-sulphonate are obtained which are stable at room temperature in absence of organic solvent by using as oxidising agent a chlorate of a group II metal of at. wt. less than that of Sr. Thus cotton or viscose rayon is printed with a paste containing Na N-phenyl-1:4-diaminobenzene-N'-sulphonate (72 g.), Ca chlorate (41),  $NH_4Cl$  (30), 1%  $NH_4$  vanadate (20), 20% ammonia (20), water and starch-tragacanth (to bring to 1000), steamed and soaped as above. This yields intense black prints.

C.O.C.

**Multicoloured Printing on a Transparent Base**

J. G. Lindmark

BP 744,738

One surface of the base is matted, e.g. by sandblasting, after which the pattern is printed on the matted surface in the reverse order to that normally used in printing on paper so that the final composite pattern when seen through the transparent base is correctly coloured.

C.O.C.

**Masked Printing Means**

Dunlop Rubber Co.

BP 743,440

A printing layer is made from a pigmented plastic composition or compositions and has embedded in it a pattern formed from material which is insoluble in a solvent for the composition. The layer is applied to the material to be printed after the composition and/or the material to be printed have been moistened with a solvent for the composition.

C.O.C.

**Printed Felt-base Floor Coverings**

Armstrong Cork Co.

USP 2,705,683

An asphalt-saturated felt base is coated on one side with a backing paint, e.g. a casein paint, and on the other side with a film containing a butadiene-styrene copolymer. After drying, a coating paint, e.g. a varnish produced by oxidising linseed oil in presence of a resin and dissolving the product in a solvent, is applied. On top of this is applied an adhesive coating paint, e.g. a filled coating in which the binder is a blend of butadiene-acrylonitrile rubber and polyvinyl chloride. The coated sheet is then block-printed on the adhesive-coated side using as the basis for the printing pastes a dispersion of vinyl chloride-vinyl acetate resin or a polyvinyl chloride resin in the form of an organosol.

USP 2,705,684

The coated felt is further coated with a composition containing  $<25\%$  of a plasticiser for vinyl resin and then block-printed with a dispersion of plasticised vinyl resin and the vinyl resin layer fused, e.g. by heating to 280-350°F.

C.O.C.

**Brown-line Prints**

D. J. Janet

USP 2,704,253

A composition for coating paper etc. for the production of brown-line prints is made by mixing dry egg albumin (6 parts by wt.) in water (36) with ammonium dichromate (3) in water (60) and with 30% aq. Toluidine Red (6).

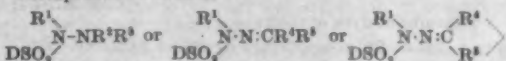
C.O.C.

**Light-sensitive Material for Photomechanical Reproduction Processes**

Kalle &amp; Co.

BP 742,557

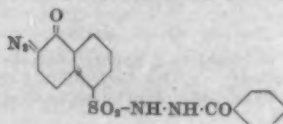
Compounds of formula —



(D = o-quinonediazide residue;  $R^1, R^2$  and  $R^3 = H$  or hydrocarbon;  $R^4 = \text{acyl}$  or Ar;  $R^5 = \text{hydrocarbon}$ ;



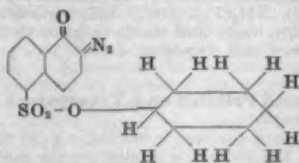
= bivalent residue of a ring system), e.g.



are suitable light sensitive materials for application to sheet aluminium. The images given by such compounds have good acceptance for greasy ink.

BP 744,987

Modification of BP 699,412 (J.S.D.C., 70, 33 (Jan. 1954)). The esters of *o*-diazophenolsulphonic acids, including *o*-diazonaphtholsulphonic acids, with cycloaliphatic acids in which the alcoholic OH group is attached to a C atom of the cycloaliphatic ring are excellently suited for producing images which may be used as stencils on printing plates. An example of such an ester is—



C.O.C.

### Photographic Colour Correction

Eastman Kodak Co.

USP 2,704,711

### Bipack Colour Film containing Non-diffusing Colour Formers

General Aniline

USP 2,705,200

A mixture of a green and red sensitive emulsion, each containing the same phenolic colour former, is cast on to a base. On top of this emulsion there are then successively coated a yellow filter layer and a blue sensitive emulsion containing an open-chain ketomethylene compound.

C.O.C.

### Precipitating Azo Dyes in Silver Halide Emulsions by Guanidine and Diguanidine Compounds containing Long Alkyl Chains

General Aniline

USP 2,704,710

### Masking Process for Multilayer Photographic Colour Film

General Aniline

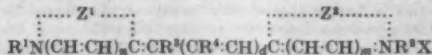
USP 2,704,709

### Mixtures of Cyanine Dyes and Unionised Dyes

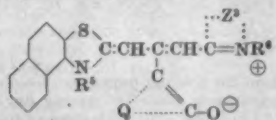
Eastman Kodak Co.

USP 2,704,714

Mixtures of dyes of formula—



( $R^1$  and  $R^2$  = Alk;  $R^3$  and  $R^4$  = H or Alk;  $d$ ,  $m$  and  $n$  = 0 or 1;  $X$  = acid radical;  $Z^1$  and  $Z^2$  = atoms to complete a 5- or 6-membered ring) e.g. 9-ethyl-1'-3-dimethylthia-2'-carbo-cyanine iodide, with dyes of formula—

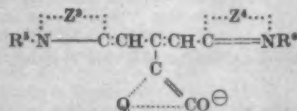


( $R^5$  and  $R^6$  = Alk;  $Q$  = atoms to complete an indandione or a 5- or 6-membered heterocyclic nucleus;  $Z^3$  = atoms to complete a 5- or 6-membered heterocyclic nucleus) e.g. 1:3-diethyl-5-[di(1-ethyl-2(1H)- $\beta$ -naphthothiazolylidene)]isopropylidene]barbituric acid, are supersensitisers the use of which yields photographic emulsions of good keeping quality.

USP 2,704,715

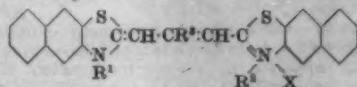
Mixtures of dyes of formula—

$R^1N(CH_2CH)_nC:CH-CR^2CH-C:(CH_2CH)_mNR^4Y$   
e.g. 3:3'-diethyl-9-phenylthiacarbo-cyanine iodide, with dyes of formula—



( $Z^4$  = atoms to complete a naphthothiazole or naphthoselenazole nucleus) e.g. 1:3-diethyl-5-[di(1-ethyl-2(1H)- $\beta$ -naphthothiazolylidene)]isopropylidene]barbituric acid, are similarly used.

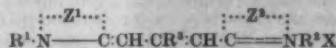
Mixtures of dyes of formula—



( $R^1$  and  $R^2$  = Alk;  $R^3$  = H or Alk;  $X$  = acid radical) e.g. 3:3'-diethyl-5:6:5':6'-dibenzothiacarbo-cyanine *p*-toluenesulphonate, are used in combination with dyes of the second type described in USP 2,704,715 (above).

USP 2,704,718

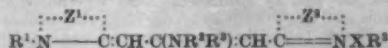
The first type of dye in the mixture is of formula—



( $R^1$  and  $R^2$  = Alk;  $R^3$  = alkoxy;  $X$  = acid radical;  $Z^1$  and  $Z^2$  = atoms to complete a 5-membered ring, a naphthothiazole, benzoselenazole or naphthoselenazole nucleus), e.g. 3:3'-dimethyl-9-methoxy-4:5:4':5'-dibenzothiacarbo-cyanine bromide.

USP 2,704,719

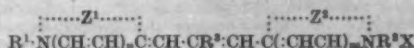
The first type of dye in the mixture is of formula—



( $R^1$  and  $R^2$  = Alk;  $R^3$  = H or acyl;  $R^4$  = H, Alk, or an aromatic or arylhydrazino group or OH if  $R^3$  = H, or  $R^3$  and  $R^4$  together = a piperidyl or morpholinyl group;  $X$  = acid;  $Z^1$  and  $Z^2$  = atoms to complete a benzothiazole or naphthothiazole nucleus) e.g. 9-anilino-3:3'-dimethylthiacarbo-cyanine *p*-toluenesulphonate.

USP 2,704,720

The first dye in the mixture is of formula—



( $R^1$  and  $R^2$  = Alk;  $R^3$  = thienyl;  $n$  and  $m$  = 0 or 1;  $X$  = acid radical;  $Z^1$  and  $Z^2$  = atoms to complete a 5- or 6-membered ring), e.g. 3:3'-dimethyl-9-(2-thienyl)-4:5:4':5'-dibenzothiacarbo-cyanine *p*-toluenesulphonamide.

C.O.C.

### Developing an Electrostatic Latent Image

H. E. Clark

USP 2,705,199

Flat xerographic plates are developed by discharging developer, e.g. a fine pigmented powder, on to them from a travelling hopper. This enables large plates, e.g. those several feet long, to be satisfactorily developed.

C.O.C.

Effect of Buffer and Electrolyte on the Diffusion of Acid Dye in Gelatin (VIII p. 188)

Blue-print and Diazotype Paper (XI p. 197)

## X—SIZING AND FINISHING

### Modern Flocking Equipment

A. Franken

Textil-Rund., 10, 593-603 (Nov. 1955)

An outline of the development of flocking processes for fabrics, paper, and other materials, and a description of modern flocking machinery operating on electrostatic principles. 16 photographs.

J.C.F.

### Removal of Water from Fabrics by Capillary Action

K. Messik, T. Bonkáló, and K. Szabó

Textil-Praxis, 11, 78-80 (Jan. 1956)

The wet material after the normal removal of water by mechanical means is placed on a J tower in contact with dry material and left for 30 min. Residual moisture in the wet material is reduced by capillary action.

B.K.

### Cellulose Fibre of Reduced Crystallinity

H. Maeda, K. Matsumoto, S. Kikuchi, and K. Uemura

J. Soc. Textile Cellulose Ind. Japan,

11, 721-727 (Nov. 1955)

Cyanoethylation of cellulose fibre in an intensely swollen state has been studied with the object of reducing the crystallinity of native cellulose. The decrystallising effect was estimated by measuring the percentage of acid hydrolysis residue. By cyanoethylation at 10°C. for 90 min. after preswelling in 8% aq. NaOH containing 2.4%

acrylonitrile at  $-5^{\circ}\text{C}$ . for 30 min., the crystallinity of purified cotton cellulose was reduced to 41.1% from the original value of 50.7%, the degree of substitution being raised only to 0.310. With such a decrystallised fibre boiling in water brought about only slight recovery in crystallinity. As a result of decrystallisation—(a) capacity for moisture and dye absorption, and swelling in water increase; (b) breaking elongation also increases, whereas breaking strength slightly falls.

AUTORS

#### Reaction between Cellulose and Formaldehyde—Influence on the Mechanical Properties of Viscose Rayon Fibres

E. M. Karrholm

*Text. Research J.*, **25**, 756–762 (Sept. 1955)

Moduli of bending, torsion, and stretching are determined for viscose rayon fibre treated with varying amounts of formaldehyde. A maximum value of all three moduli is obtained at about 5% fixed formaldehyde. The results suggest that the number of cross-links increases as the amount of formaldehyde increases up to 5%. At higher values the length of the cross-links increases. Formaldehyde polymers, soluble in sodium sulphite solution, may considerably modify mechanical properties. W.R.M.

#### Reaction of Cellulose with Bis- and Mono-hydroxymethylureas (Di- and Mono-methylolureas)

R. Steele and L. E. Giddings

*Ind. Eng. Chem.*, **48**, 110–114 (Jan. 1956)

Monomethylolurea is monofunctional with respect to cellulose. When applied to cotton and viscose rayon fabrics, analysis and solubility measurements show that it forms chains three or four urea residues long which appear to be attached at one end to the main cellulose chains. Dimethylolurea and other precondensates of formaldehyde: urea ratio approx. 2:1 are difunctional, and form cross-links about two urea residues long between the cellulose chains. On rayon, with up to 6% resin content, the dimethylol product provides only slightly better crease resistance than the monomethylol product, but on cotton it is much more effective. This difference is attributed to the difference in chemical accessibility of the fibres and the resulting difference in effective resin concentration. The reaction of urea-formaldehyde resins occurs in two stages: the small amount of resinification occurs during drying, and the reaction with cellulose occurs on curing at higher temperature. Acid catalysts promote the reaction with cellulose rather than resinification. W.K.R.

#### Catalysis of Urea-Formaldehyde Condensation

I. J. Grunfest and E. M. Young

*Ind. Eng. Chem.*, **48**, 107–109 (Jan. 1956)

Certain cationic acids such as the pyridinium ion do not catalyse the urea-formaldehyde reaction in the presence of water, but do so when the water is removed, and thus act as latent catalysts without impairing the stability of the precondensate. Many amine ions having acid dissociation constants in water between  $10^{-7}$  and  $10^{-4}$  are effective catalysts, though carboxylic acids of the same strength are ineffective. Catalytic activity is reduced or destroyed under conditions where intramolecular neutralisation or cyclisation with formaldehyde can occur. The use of this type of catalyst is illustrated by the results of the application of a urea-formaldehyde precondensate to paper. Increased wet strength was attained rapidly after drying at room temperature. W.K.R.

#### Melamine Resins in Textile Finishing

J. Müller and F. Liewald

*Z. ges. Textilind.*, **58**, 25–29 (5 Jan. 1956)

Details are given for the application of two hydroxymethylmelamines, Cassuril MKF conc. pdr. and MLP liquid (CFM), for the production of chintz and other permanent calendar finishes and crease-resist finishes on cotton and spun viscose rayon staple, and also wash-fast finishes including stiff finishes on synthetic fibres. B.K.

#### Catalytic Degradation and Oxidation of Cellulose

W. G. Parks, M. Antoni, A. E. Petrarca, and A. R. Pitochelli

*Text. Research J.*, **25**, 789–796 (Sept. 1955)

Thermal decomposition products of cellulose treated with organophosphorus compounds are studied. A comparison is made between amounts of char and tar produced, and a correlation between the  $\text{CO}/\text{CO}_2$  ratio and the afterglow

exhibited by treated cotton is obtained. The results support the theory that fire-resistant cellulose produces less tar and more  $\text{CO}$  than untreated cellulose. A method is given for determination of water, non-aqueous volatile products, char, and tar resulting from pyrolysis of cellulose. A large part of the gaseous products from pyrolysis are non-aqueous. The data tend to support a dehydration mechanism for the action of fire-resistant compounds on cotton. W.R.M.

#### Digestibility of Chemically Modified Wools in Papain-Bisulphite-Urea

F. G. Lennox

*Text. Research J.*, **25**, 676–682 (Aug. 1955)

The digestibility of wool in papain-bisulphite-urea is increased by prior treatment with cold conc. sulphuric acid, nitrous acid, or iodine, but is diminished by 1-fluoro-2,4-dinitrobenzene, formaldehyde, chromium compounds, epichlorohydrin, propylene oxide, methyl iodide at pH values above 6, thiocyanate with acetic anhydride at pH below 6, and, if applied to the reduced fibre, by 1,3-dibromopropane, acrolein, and methyl iodide at pH above 7. Treatment with acid solutions of various aliphatic alcohols to esterify the carboxyl groups in wool likewise reduces the digestibility, maximum protection being obtained with methanol. The results are discussed in relation to the chemical reactions of the reagents with the protein. W.P.M.

#### Improvement of the Quality of Silk by Chemical Treatments. III—Treatment of Silk with Carbazide

M. Nakanishi

*J. Soc. Textile Cellulose Ind. Japan*, **11**, 740–744 (Nov. 1955)

Two methods for preventing the autoxidation of silk are discussed—the blocking of the phenolic hydroxyl groups of tyrosine and the fixation of an autoxidising agent on the silk fibre. Silk treated with thiosemicarbazone (from thiosemicarbazide and formaldehyde) is compared with that treated with semicarbazone. It is concluded that thiosemicarbazide is remarkably effective in preventing the autoxidation of silk, but semicarbazide is ineffective. AUTHOR

#### Resin Finishing of Silk Fabrics

A. Kuwahara

#### IV—Treatment of Silk Crêpe with Acrylate Monomers

*J. Soc. Textile Cellulose Ind. Japan*, **11**, 802–805 (Dec. 1955)

The changes in quality of silk crêpe treated with various acrylate monomers (methyl, ethyl, and butyl acrylate) have been studied. Tensile strength, elongation, stiffness, resilience, and variation of tensile strength under ultraviolet radiation have been compared—

(1) The higher the number of carbon atoms in the acrylate monomer and the greater its concentration, the greater becomes the value of the resin for the flat crêpe.

(2) The resin finishing of cloth is not so much effective for elongation development as for tensile strength development.

(3) Fall in tensile strength under ultraviolet rays is more marked when less resin is combined.

(4) Among the samples examined, the stiffness after treatment with butyl acrylate was excellent, but they could be improved slightly in resilience.

Butyl acrylate is preferable to other acrylate monomers for the maintenance of silky feel and the improvement of quality by resin finishing.

#### V—Relation of Resin Finishing to Weakening and Resistance

*Ibid.*, 805–808

The relation of resin finishing with weakening and resistance of silk crêpe was studied by determination of tensile strength, elongation, yellowing by ammonia gas, and variation of absorption coefficient through exposure to ultraviolet rays of crêpe treated with various resins (polyethyl, butyl acrylate, polyvinylbutyral, polystyrene emulsion, and resin formed in fabrics by ethyl, butyl acrylate monomers). In tensile strength, yellowing by ammonia gas treatment, and the absorption coefficient, butyl acrylate is superior to other resins. But the acrylate monomers yellow more than the polymer emulsions on treatment with ammonia gas. AUTHOR



## PATENTS

**Permanently Crimped Synthetic Fibres**

Heberlein &amp; Co.

BP 744,735

Temporary high twist is imparted by a false-twisting device to yarns of synthetic organic fibres having normal or no twist. The yarns are then treated for 2–30 sec. in gas at 150–300°C. below the m.p. of fibres and are then cooled.

BP 744,736

The yarn is treated for 0.1–20.0 sec. in steam at < 30 lb. pressure.

BP 744,737

Suitable apparatus is described.

C.O.C.

**Reducing the Felting Power of Wool Yarn or Fabric**

Cluett, Peabody &amp; Co.

USP 2,704,729

A mixture of a butadiene polymer and a butadiene-acrylonitrile copolymer is especially good for application to wool to reduce its felting power. Thus wool fabric treated with 4% of butadiene-acrylonitrile had its shrinkage reduced by < 10%; treated with 1% polybutadiene the reduction was 11%; treated with 5% of a 4:1 mixture of the two polymers the shrinkage was reduced by 31%.

C.O.C.

**Imparting a Softer Handle to Wool**

Maifoss

BP 744,469

The wool is treated at or near to the boil in an aqueous liquid containing an acid or an ammonium salt and a water-soluble condensate of urea or formaldehyde with an aromatic sulphonic acid or sulphonate, e.g. Paralene 23344 (YDC) at pH < 5.5, the amount of condensate being > 0.5% on the weight of the wool.

C.O.C.

**Sizing Cellulosic Sheets**

Union Carbide &amp; Carbon Corp.

BP 744,093

Paper or cotton cloth is treated with an aqueous mixture containing starch, a water-soluble ketone-formaldehyde condensate and alkali to bring the mixture to pH > 10 and is then heated in steam to render the mixture insoluble. The cloth can be bleached or dyed immediately after being steam cured, no intermediate drying being necessary. Thus cotton cloth was kier boiled, rinsed, treated with an aqueous mixture of starch and acetone-formaldehyde precondensate, steamed for 60 min. at 105°C., washed with water, peroxide bleached, dried in absence of tension and calendered. The finished cloth had a pleasant wash-resistant finish and shrinkage of < 3% on boiling.

C.O.C.

**Fibrous Web Impregnated with a Heat-resistant Phenol-Aldehyde Condensate**

N. V. Philips Gloeilampenfabrieken

BP 743,623

The material, e.g. paper or cloth, is impregnated with an aqueous emulsion of a phenol-aldehyde precondensate, the emulsion being of such type that it has to be constantly agitated to prevent it settling, after which the impregnated material is treated to harden the resin. This allows very wide choice of the phenol-aldehyde condensate to be used.

C.O.C.

**Finishing Fabrics with Synthetic Resins**

Joseph Bancroft &amp; Sons Co.

BP 742,885

The fabric is impregnated with an aqueous resin-containing preparation and polyvinyl alcohol in absence of unreacted aldehyde or other component tending to react preferably with the alcohol. It is then dried and baked at 250°F. long enough to copolymerise the resin and alcohol to an insoluble form. This results in a finish which will last for the whole life of the fabric.

C.O.C.

**Coloured and Embossed Effects on Synthetic Thermoplastic Materials**

Radner &amp; Co.

BP 744,177

Thermoplastic material consisting of linear macromolecules containing other atoms beside carbon in the main chain is embossed at 30–60°C. below its m.p. The material is treated before embossing with an agent which neither shrinks nor swells it and which has b.p. above the temperature of embossing and which is liquid at that temperature. It is then dyed. Thus desized and bleached nylon mousseline (m.p. 240°C.) is padded with a 30% aqueous solution of urea, mangled and dried at 60°C. It is then passed at 8 yd. per min. between a nip formed by an upper engraved steel cylinder heated to 195°C. and a cold paper bowl, the pressure of the nip being 8 tons. The

embossed portions have increased affinity for dyes, especially acid dyes, and they have increased lustre. Rinsing the fabric and acid dyeing results in tone-in-tone effects combined with local gloss.

C.O.C.

**Patterned Mechanical Finish on Thermoplastic Sheets or Fabrics**

Cilander

BP 742,295

A heat-insulating resist is applied to the fabric or sheet before treatment with a heated forming member. Thus nylon pereale is printed with a paste of gum arabic (450 g.), water (540), and turpentine (10). It is then lustre calendered at 150°C. after which the resist is washed out. This results in a less-glazed pattern on a high-glazed ground. In another example spun nylon fabric is printed with acetyl cellulose (185 g.) and acetic ester (115). It is then calendered at 140°C., the resist removed with acetone and the fabric roller embossed at 140°C. This results in lustred unembossed places (areas not printed with the resist), delustred unembossed places (areas printed with the resist), lustred embossed places (areas not printed with the resist) and embossed places of lower lustre (areas printed with the resist).

C.O.C.

**Increasing the Resistance of Fabrics to Water, Gas-fume Fading, and Fire**

Phillips Petroleum Co.

BP 744,244

The fabric is impregnated with a homo- or copolymer of a pyridine derivative containing one or more vinyl groups. Preferably an aqueous acid solution of the polymer is used after which the impregnated fabric may be treated with an aqueous alkaline solution so as to liberate the free polymeric base. This imparts water-repellency and resistance to gas fume fading. The finish is fast to laundering and dry cleaning.

C.O.C.

**Rotproofing**

Monsanto

BP 743,408

The materials are treated with an aqueous solution containing a salt of an aromatic hydroxy compound having antimildew properties, e.g. salicylanilide, a bactericidal quaternary ammonium salt, e.g. cetylpyridinium bromide, and, as stabiliser, a surface-active alkyleneoxide condensate or an alkali metal or ammonium salt of a formaldehyde-aromatic sulphonic acid condensate, e.g. Lubrol W (ICI) or Lissatan AC (ICI). The stabiliser prevents the two components from being precipitated as a water-insoluble complex.

C.O.C.

**Rotproofing**

S

BP 742,812

Textiles, particularly cellulosic textiles, animal skins, etc. rotproofed with compounds of formula R-Hg-X (R = mononuclear aromatic radical; X = anion), e.g. phenylmercury triethanol ammonium salts, have the rotproof finish made resistant to the action of moisture by treating them with solutions or dispersions of basic nitrogenous condensates which form complexes with the chemically bound mercury, e.g. the product obtained by warming dihydramide (9 g.), NH<sub>4</sub>Cl (9 g.), distilled water (18 c.c.) and 37.8% aq. HCHO (27 c.c.) under reflux until a homogeneous solution is obtained. This is then boiled under reflux for 28 min., and evaporated under vacuum at 60–65°C. If desired the mercury compound and the nitrogenous condensate can be applied in the same liquor.

C.O.C.

**Combined Cleansing and Sizing of Carpets and Pile Fabrics**

T. F. Firth &amp; Sons and ICI

BP 744,891

The fabric is treated with a volatile solvent for grease and then, without being dried, with a size which is soluble in the solvent. Thus carpeting from the loom passes through a series of tanks containing trichloroethylene which flows from one tank to the other in the opposite direction to the carpeting. On leaving the last tank the carpeting passes through squeegee rollers and then over slotted suction pipes and then over a roller which applies size, e.g. a 35% by wt. soln. of CaZn resinate in trichloroethylene. The suction and the size are applied to the back of the carpeting.

BP 744,892

A machine based on the above principle consists of three closed compartments in one of which the carpeting is



treated with a solvent, in another with the size and is dried in the third. They are so constructed and arranged that the processing is continuous. C.O.C.

#### Coating Moving Web with Liquids

Jagenberg-Werke

BP 743,768

The coating liquid is applied by any suitable means to the cloth or other web. A jet of compressed air is directed into the web to adjust the thickness of the coating, the air jet preventing excess of the coating liquor being taken up by the web and at the same time smoothing the coating liquor left in the web so that an uninterrupted coating of uniform thickness is obtained. C.O.C.

#### Semi-porous Coated Cloth

H. Glat

USP 2,704,730

Fabric useful as interlinings, ironing pad covers, etc. is obtained by knife coating a base fabric with a liquid containing a dissolved and/or dispersed plastic material in it. This deposits most of the plastic in the interstices of the cloth yielding a smooth surface with high reflective power. C.O.C.

#### Imparting Dimensional Stability to Pile Fabric the Backing of which is made from Thermoplastic Fibres

George W. Borg Corp.

USP 2,705,880

A pile fabric the backing of which is made of thermoplastic fibres is treated on the back so as to release the internal tension in the thermoplastic fibres, e.g. by heating, while maintaining the backing under constant tension. This imparts dimensional stability to the backing. C.O.C.

#### Water-repellent Finish on Garments, etc.

Davies-Young Soap Co.

USP 2,704,731

A non-aqueous solution of a resin or wax floats upon water. A highly electrically conductive, horizontal stationary grid is placed a little way above the surface of the water. This grid is earthed. The article to be treated is immersed in the resin or wax solution, the immersion and removal of the article being sufficient to effect movement of the solution and the water and so cause a small amount of the water to disperse through the grid. This makes the solution conductive of static electricity so that any electric charge formed leaks through the grid to earth. C.O.C.

#### Permanently Waving or Straightening Human Hair

J. V. Morelle

BP 743,730

A composition containing a thiolactate and a water-soluble gel-forming substance is used, e.g. an aqueous composition made up of casein and ammonium thiolactate. C.O.C.

#### Non-woven Fabric

Chicopee Manufacturing Co.

USP 2,705,686

A carded lap the greater proportion of whose fibres are oriented predominantly in one direction has adhesive applied to it in the form of numerous rings (which may be circular, triangular or hexagonal, etc.) arranged in non-overlapping columns parallel to the direction of fibre orientation. The individual rings are connected by the oriented fibres so as to form interconnected parallelograms that are collapsible on the "lazy tongue" principle. The area covered by adhesive is < 35% of the area of the lap. C.O.C.

The binder is applied in an articulated multi-segmented pattern, a large proportion of the segments being at an angle to the direction of fibre orientation. C.O.C.

The rings of binder are applied in parallel rows across the lap, each row being staggered in relation to those on either side of it. C.O.C.

Two carded laps of oriented fibres, the direction of orientation in one lap being at an angle to that in the other, are bonded together by numerous discrete areas of binders, these areas being arranged to coat with the fibres to form interconnected geometric figures that collapse when the finished web is extended in one direction and recover their shape when the stretched fabric is extended in the other direction. C.O.C.

#### Intermediate for Flame-resistant Polymers—Reactions of Tetrakis(hydroxymethyl)phosphonium Chloride (III p. 174)

Crease Resistance of Mixed (Amilan-Viscose Rayon)

Fabrics (VI p. 184)

Cellulose Thiourethans (VI p. 186)

Bleaching Wool with Simultaneous Reduction in Felting Power (VII p. 187)

Rayon in Tufted Carpeting (VIII p. 188)

Advances in Dyeing and Finishing Man-made Fibres (VIII p. 189)

Printed Felt-base Floor Coverings (IX p. 191)

Changes in the Fibre Structure of Wood Pulp during Cold Purification with Caustic Soda and Subsequent Drying (XI below)

Colouring Cellulosic Materials by Hot Embossing (XI p. 197)

Imparting a Slip Finish to Vinyl Resin Sheet (XIII p. 199)

## XI—PAPER AND OTHER CELLULOSIC PRODUCTS

### Wet Strength of Paper. XIII—Effects of Hemicellulose on the Heat Treatment of Paper

I. Yoshino, S. Senda, and Y. Sumikawa

*J. Soc. Textile Cellulose Ind. Japan,*

11, 732-736 (Nov. 1955)

The wet strength of paper is increased by heat treatment. Paper was coated with raw xylan obtained from beech sawdust or with the mannan-rich hemicellulose extracted from unbleached spruce kraft pulp. When these coated papers were subjected to heat treatment, no increase in wet strength was observed in comparison with the uncoated paper. On the other hand, when the papers made from bleached kraft pulp which had been pre-extracted with NaOH solutions of different concentrations were heated, then the greater their hemicellulose content, the more their wet strength developed. Especially, the maximum values of the wet strength obtained by heat treatments at a comparatively low temperature, ca. 130°C., were found to be proportional to the hemicellulose content of the papers. From these facts it may be assumed that a part of the increase in wet strength on heat treatment, which is notably more sensitive to heat than the remaining part, is due to the hemicellulose contained in the original fibre. This assumption is also supported by the results of treatment in boiling water, buffered to the neutral pH. It may be concluded that the hemicellulose contained in the original fibre is effective, but it is quite ineffective when once it has been extracted by alkali. An explanation may be given as follows: the hemicellulose is strongly held in the fine structure of the cellulose fibre. This structure is relaxed by heating, and dipole-dipole bonding is developed between the cellulose and the hemicellulose chain. Thus, finally a hydrogen bond is formed between fibre and fibre. Between the cellulose fibre and the hemicellulose, once it has been extracted by alkali, no such strong bindings will be formed. AUTHORS

### Changes in the Fibre Structure of Wood Pulp during Cold Purification with Caustic Soda and Subsequent Drying

T. Yurugi

*J. Soc. Textile Cellulose Ind. Japan,*

11, 736-740 (Nov. 1955)

Changes in the fibre structure of cellulosic materials, such as degree of crystallinity and lateral order and system of cavities, during cold extraction with caustic solutions of various concentrations and during subsequent drying under various conditions, have been investigated experimentally. It has been found that if cellulosic materials are treated with caustic soda solutions of over certain concentrations, the amount of amorphous material increases at the expense of highly ordered material. These limiting concn. are at 20°C. 10-12% for cotton linters and 8-10% for wood pulp. The increased amorphous region, if dried below 80% R.H., becomes "horny" and loses its capacity for reaction, which is completely recovered on wetting with water. Lateral order distribution was estimated from the solubility of the residue in caustic soda of various concn. after the levelling-off D.P. had been attained by acid hydrolysis. Relative pore sizes of fibre texture were determined by measuring the dye-uptake from unswollen medium. AUTHOR

**Kinetics of Xanthation**

M. Wronski

*J. Polymer Sci.*, 19, 210-212 (Jan. 1956)

A simplified theory, assuming a constant concentration of carbon disulphide and reaction in a single phase, is advanced to account for the kinetics of xanthation of soda cellulose.

W.R.M.

**Theory of Viscose Ripening**

M. Wronski

*J. Polymer Sci.*, 19, 212-213 (Jan. 1956)

It is concluded that the influence of the concentration of NaOH is complex. A decrease in the concentration of carbon disulphide increases the velocity of ripening.

W.R.M.

**Rôle of the Hydrogen Bond in the Rheological Behaviour of Cellulose Sheets**

A. H. Nissan

*Text. Research J.*, 25, 780-788 (Sept. 1955)

Some properties of cellulosic sheets are discussed in terms of the author's theory of the rôle of the hydrogen bond. Basic elements of the theory are given together with the elucidation of the characterisations of the hydrogen bond from the mechanical properties of sheets.

W.R.M.

**Cellulose Studies. XX—Comparison of Polymolecularity of Celluloses degraded by Acid Hydrolysis and by Alkali Ageing**

Y. Siegart, L. Rebenfeld, and E. Pacsu

*Text. Research J.*, 25, 1001-1004 (Dec. 1955)

Samples of wood pulp cellulose (original D.P. 940), (I) degraded by acid hydrolysis (N-HCl, 130 min., 60°C.) and (II) by alkali ageing (65 hr. at room temp.), were found to have approx. the same D.P. (ca. 425). The degraded samples were nitrated and dissolved in acetone (1% soln.). Molecular-weight distributions were obtained by fractional precipitation with water. I gave a distribution curve with a single maximum slightly lower than the average D.P. and pronounced positive skewness. The distribution curve of II was quite different, and showed two distinct maxima at D.P. 400 and 600. This mol.-wt. distribution must be considered in formulating a mechanism for the alkali ageing process.

J.C.F.

**Effect of Various Treatments on the Hydrolysis of Cellulose**

D. V. Zharkovskii and S. M. Lipatov

*Izvestiya Akad. Nauk Belorus. S.S.R.*, (5), 115-124 (1953)*Chem. Abs.*, 49, 11271 (25 Aug. 1955)

Cotton cellulose is ground to an average particle size of 50  $\mu$ , and the original and ground preparations are subjected to single- and multi-stage hydrolysis with 0.5 N-H<sub>2</sub>SO<sub>4</sub> for periods ranging up to 7 hr. The ground cellulose hydrolyses 8-10 times as fast as the original. In the stepwise hydrolysis of the celluloses, the solubilities of the residues and the yields of sugar decrease greatly in each successive stage; this is attributed to recrystallisation during drying at 105°C.

A.E.S.

**Relation between Water Sorption and Swelling of Regenerated Cellulose Film**

Kh. U. Usmanov and Ya. V. Pak

*Doklady Akad. Nauk Uzbek. S.S.R.*, (12), 25-28 (1953)*Chem. Abs.*, 49, 11273 (25 Aug. 1955)**Alcoholysis of Cellulose**

R. B. Valley

*Text. Research J.*, 25, 930-939 (Nov. 1955)

Alcoholysis of cotton linters is studied, using methanol, 1-butanol, 1-hexanol, and 1-octanol acidified with HCl. The linters are degraded in each case. The amount solubilised during degradation tends to increase with the molecular weight of the alcohol. It appears that degradation results from hydrolysis caused by traces of water. The acidified alcohols combine with reducing groups to give a degraded cellulose with a low reducing value. The residual reducing power is least when methanol is used.

W.R.M.

**Differentiation and Determination of Carbonyl Groups in Oxycelluloses—Application to Oxycelluloses produced by Hypobromite Oxidation**

J. Meybeck and M. El Ghoroury

*Bull. Inst. Text. France*, (57), 25-41 (Dec. 1955)

The authors discuss the various methods available for the differentiation and estimation of the various types of carbonyl groups present in oxycelluloses. In particular, the following methods have been applied in the investigation of oxycelluloses produced by hypobromite oxidation at various pH values—(a) copper number, (b) total carbonyl groups by condensation with NH<sub>2</sub>OH.HCl and titration of the HCl liberated, (c) aldehyde groups by oxidation with acid chlorite and estimation of the carboxyl groups produced, and (d) solubility in aq. NaOH. Oxycelluloses produced by oxidation at pH 8 and pH 13 showed clearly differentiated properties. At pH 8, the oxycelluloses produced showed a high reducing power (true aldehyde groups 40-45% of total carbonyl groups), relatively low carboxyl content, and a small decrease in D.P. At pH 13, the oxycelluloses produced showed a low reducing power (aldehyde groups 4% of total carbonyl groups), a relatively high carboxyl content, and a marked decrease in D.P. The pH 13 oxycelluloses possessed a greater resistance to alkali, in agreement with the low content of aldehyde groups.

J.C.F.

**Phase Structure of Hydrate-cellulose Films**

V. A. Kargin, V. L. Karpov, Yu. S. Lipatov, G. S. Markova, and T. A. Koretskaya

*Doklady Akad. Nauk S.S.S.R.*, 101, 707-709 (1 April 1955)

Hydrate cellulose is prepared in the form of thin films by denitration of cellulose nitrate with aq. NaHS, hydrolysis of cellulose acetate with aq. NH<sub>3</sub>, and regeneration of cotton cellulose from cuprammonium soln. After being washed for several days, the films generally retain some crystalline occlusions, which give rise to sharp rings in diffraction images obtained with 57- and 90-kv. electron beams. The positions of the rings correspond to the presence of ammonium acetate in hydrolysed cellulose acetate and of sulphur in denitrated cellulose nitrate. When such occlusions are absent, only diffuse halos are obtained. It is concluded that the sharp diffraction rings observed by Zaides and Stoyanova-Sinitakaya (see J.S.D.C., 70, 212 (1954)) and others, which were interpreted by these authors as evidence for the presence of microcrystalline phases in hydrate cellulose, must be attributed merely to the presence of impurities in their preparations.

A.E.S.

**Synthesis of Benzylcelluloses in presence of Xylene**

E. N. Lyubimova

*J. Appl. Chem. U.S.S.R.*, 28, 1220-1224 (Nov. 1955)

In the treatment of alkali-cellulose containing various amounts of caustic soda with benzyl chloride, improved yields and increased degree of substitution (up to 2 benzyl groups per glucose residue) can be attained by addition of xylene, which is particularly effective at high alkali concn.

A.E.S.

**Celluloid**

Y. Matsuda

**I—Influence of Nitration Temperature and Time on the Viscosity of the Solution and the Mechanical Properties of the Film made from the Cellulose Nitrate used for Celluloid**

*J. Soc. Textile Cellulose Ind. Japan*, 11, 822-827 (Dec. 1955)

**II—Influence of the Nitration Temperature and Time on the Transparency (Turbidity) of the Solution and the Yield of the Cellulose Nitrate used for Celluloid**

*Ibid.*, 827-829**PATENTS****Paper of Improved Dry and Wet Strength**

Harold Jackson

BP 743,262

The dry and wet strengths of paper are improved by adding to the stock before sheet formation, particularly at the beater, 1% or more of insolubilised gel, dispersed in water, prepared from a mixture of joinder's glue and Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (or other trivalent Cr salt) with or without addition of an aq. dispersion of rubber latex or other high

polymer, e.g. polyvinyl acetate and polyvinyl chloride. Other advantages are high retention of the glue by the pulp, the pH of the stock need not be lowered on beater application, and incorporation of the latex or other polymers into the stock is facilitated. K.W.

#### Aqueous Dispersions of Cellulosic Materials or Cellulose Derivatives and Fibres, Films, etc. produced from them

DuP

BP 743,923

Cellulosic films or fibres are prepared, without substantial degradation of the cellulose or requiring additional chemicals and disposal of waste products, by dispersing at 25°C. finely ground cellulosic materials, e.g. purified wood pulp or cotton linters, or cellulose derivatives, in amounts of 9 to 30% in 40–74% aq. Ca(SCN)<sub>2</sub>. The non-pourable dispersion obtained can be converted into a gel and formed into films or fibres by pressing, calendaring or extruding at temperatures of 100–150°C. under elevated pressures. The strength and clarity of the films are improved by immersion in coagulating baths containing aq. salt solutions, preferably 25% aq. NaCl. K.W.

#### Colouring Cellulosic Materials by Hot Embossing

American Cyanamid Co.

USP 2,705,682

Paper or other cellulosic material is coated with a mixture containing a pigment which is insoluble in both water and oil, a binder, e.g. casein, a wax emulsion and an oil-soluble colouring matter. The oil-soluble colouring matter does not normally affect the overall colour of the coated material, until both heat and pressure are applied. C.O.C.

#### Coating Strip Material and Producing Foils

Unilever

BP 742,761

The strip material, such as paper or board, on which the coating substance, preferably thermoplastic, has been placed as a solution, dispersion, or solid passes on a support or an endless conveyor past a doctor blade that is vibrated electromagnetically, at least 50 cycles/sec., along its longitudinal axis transversely to the moving strip. The blade may be made of rubber, or of metal if it is to be heated by electric resistance. The heated, vibrating doctor blade may be applied for forming foils from thermoplastic materials placed on an endless conveyor. K.W.

#### Blue-print and Diazotype Paper

Kalle &amp; Co.

BP 742,407

The paper is coated with an aqueous suspension of a silicate of a Group II metal especially of Mg or an alkaline earth metal and then with the light sensitive material. The silicate particles must not be > 5 μ. Such paper yields prints showing excellent contrast and has greater fastness to ink and Indian ink and is more receptive of water colours than previous papers pre-coated with silicic acid. C.O.C.

#### Thermally Stabilised Cellulose Acetate Compositions

Hercules Powder Co.

BP 744,060

Aliphatic cellulose ester compositions containing combined sulphate groups can be thermally stabilised by incorporation of a small proportion of an epoxide, e.g. Epon RN-48 (Shell) and a sulphuric acid neutralising-type stabiliser, e.g. CaCO<sub>3</sub>, the latter being usually incorporated by adding it to the wash water used after esterifying the cellulose. C.O.C.

#### Phosphate Plasticisers imparting Fire-retardant Properties to Thermoplastic Cellulose Derivatives

Celanese Corp. of America

BP 743,922

Bis-dipropylphosphates of alkylene or mono-oxa-alkylene glycol (glycol of 4–8 C), e.g. butanediol-1:4-bis-dipropyl or diethyleneglycol-bis-dipropylphosphate are plasticisers for thermoplastic cellulose derivatives to which they also impart fire-retardant properties. The esters of alkylene glycols have better resistance to water than those of mono-oxa-alkylene glycols. C.O.C.

#### Tough, Flame-resistant, Dimensionally Stable, Heat-stable Cellulose Derivatives or Vinyl Resin Plastic Compositions

Hercules Powder Co.

BP 744,051

A halogenated aliphatic phosphate is used as the plasticiser together with enough of a resinous non-volatile epoxide to confer stability to heat. The epoxide is obtained by condensing epichlorohydrin with bis(4-hydroxyphenyl)-2:2-propane so that the product contains > 1 epoxy group. C.O.C.

Modern Flocking Equipment (X p. 192)

Cellulose Fibre of Reduced Crystallinity (X p. 192)

Catalysis of Urea-Formaldehyde Condensation (X p. 193)

Sizing Cellulosic Sheets (X p. 194)

## XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

PATENT

#### Tanning

Boehme Fettechemie

BP 745,000

Artificial resins containing the group—



the basic groups of which have formed salt groups with an acid have considerable affinity for collagen and are excellent tanning agents. They can be insolubilised in the leather, e.g. by forming the free resin base or by treating with suitable acids or salts. C.O.C.

## XIII—RUBBER; RESINS; PLASTICS

#### Dependence of the Rates of Adsorption of Polymers by Active Carbon on their Molecular Weights

A. I. Yurzenko and I. I. Maleev

Doklady Akad. Nauk S.S.S.R.,

103, 1037–1059 (21 Aug. 1955)

The rates of adsorption of certain polymers (polystyrene, polyisoprene, butadiene-styrene copolymer) by active carbon from soln. vary greatly with the identity of the solvent and of the polymer, but for each polymer in a given solvent the time required for complete adsorption is proportional to the square of the intrinsic viscosity of the polymer. This fact can be made the basis of a method of fractionation. A.E.S.

#### Utilisation of the Amino Acids of Silk Protein

N. Hojo, M. Imoto, and H. Hirabayashi

##### I—Preparation of Tyrosine Resin

J. Soc. Textile Cellulose Ind. Japan,

11, 816–820 (Dec. 1955)

In order to utilise the amino acids in silk protein, the authors synthesised ion-exchange resins with these acids. From the structural point of view, tyrosine is considered a good basis for amphoteric resins. Synthetic tests were made of the following with acid or alkaline catalysts—(1) tyrosine + HCHO, (2) tyrosine + phenol + HCHO, and (3) tyrosine + resorcinol + HCHO. A good resin is obtained from tyrosine, phenol, HCHO, and NaOH as catalyst. This resin is not soluble in water, acids, or alkali, and is mechanically stable enough to be of practical value. The resin which is produced from tyrosine (1), phenol (2), and formalin (3) has an exchange capacity of 2.18 m-equiv. cation per gram and 1.75 m-equiv. anion per gram. The pH titration curves of these resins show that the quantity of amino group decreases and a new group appears.

##### II—Properties of Tyrosine-Phenol Resins

Ibid., 820–822

Tyrosine-phenol resins are compared with anthranilic acid-phenol resins for their adsorption of metallic ions—Co<sup>2+</sup>, Hg<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>—from solutions of differing pH.

AUTHORS



### Depolymerisation of Polycaprolactam by Alkali-metal Carbonates

O. Wichterle, J. Sebenda, and J. Králíček  
*Faserforsch. und Textiltech.*, **6**, 563-566 (Dec. 1955)

A depolymerisation process for recovery of pure lactam from soiled polyamide wastes is described. Experimental results are given showing advantages and disadvantages of alkali-metal carbonate depolymerisation and some practical applications. W.R.M.

### Properties of Binary Mixed Polyamides

V. V. Korshak and T. M. Frunze  
*Doklady Akad. Nauk S.S.S.R.*, **103**, 623-626 (1 Aug. 1955)

A summary is given of the author's work on polyamides obtained by the co-condensation of two components, each of which is either a diamine salt of a dicarboxylic acid (or the equivalent mixture of base and acid), an  $\omega$ -aminoalkanoic acid, or a lactam of an  $\omega$ -aminoalkanoic acid (see J.S.D.C., **71**, 479 (1955), **72**, 128 (March 1956)). A.E.S.

### Macromolecular Compounds

#### XLVIII—Kinetics of the Polycondensation of 2-Aminoethanol with Sebacic Acid

G. N. Chelnokova and V. V. Korshak  
*Sbornik statei po obshchei khim.*, **2**, 1070-1074 (1953)

The course of the polycondensation of 2-aminoethanol with sebacic acid at 120-160°C. is followed by determining the amounts of terminal  $\text{NH}_2$ , OH, and COOH groups present in the system after various periods of time. The COOH groups react much more rapidly with  $\text{NH}_2$  groups than with OH groups. The OH groups react according to a second-order kinetic equation, and the overall reaction of the COOH groups is expressed by a third-order equation.

#### XLIX—Peculiarities of the Reactions of 2-Aminoethanol with Adipic and Sebacic Acids

G. N. Chelnokova, V. V. Korshak, and S. R. Rafikov  
*Ibid.*, 1075-1080

In order to obtain more data relating to preferential amide formation in the reaction between 2-aminoethanol (I) and a dicarboxylic acid—observed in the polycondensation of I with sebacic acid (see above)—a study is made of the reaction between I and adipic acid at a molar ratio of 2:1. At 150-180°C.  $\text{NN}'$ -bis-2-hydroxyethyladipamide is obtained in high yield, and this substance will not condense further when heated alone. Under these conditions reaction between COOH and  $\text{NH}_2$  is 18 times as fast as that between COOH and OH, whereas at 119°C. the ratio of the reaction rates is only 2-8.

#### L—Mechanism of the Polycondensation of 2-Aminoethanol with Dicarboxylic Acids

V. V. Korshak, G. N. Chelnokova, and G. I. Distler  
*Ibid.*, 1278-1283

Polycondensation of 2-aminoethanol (I) with adipic or sebacic acid at a molar ratio of 1:1 gives a poly(amide-ester) that is substantially free from terminal amino groups, the terminal groups being COOH and OH. Reaction of sebacic acid (II) with  $\text{NN}'$ -bis-2-hydroxyethylsebacamide at a molar ratio of 1:1 gives a polymer that is identical in properties with that obtained by the direct condensation of I and II at a molar ratio of 1:1. Electron-diffraction analysis shows that these two polymers have identical longitudinal spacings of 16-9 Å., corresponding to a repeating unit of  $[\text{O}-(\text{CH}_2)_4-\text{NH}-\text{CO}-(\text{CH}_2)_8-\text{CO}]$ . It is concluded that exchange reactions play an important part in the polycondensation process. A.E.S.

### Multicomponent Polyamides

V. V. Korshak and T. M. Frunze  
*Doklady Akad. Nauk S.S.S.R.*, **103**, 843-846 (11 Aug. 1955)

The authors' work on multicomponent polyamides is summarised. Part of it has been described in detail (see J.S.D.C., **72**, 128 (March 1956); LXXV), but the present account covers a wider range of mixed polymers. The components of the ternary and quaternary monomer mixtures are selected from hexamethylenediamine adipate, azela-to, and sebacate; 6-hexanolactam; and 7-amino-

heptanoic, 9-aminononanoic, and 11-aminoundecanoic acids. Triangular m.p.-composition diagrams are given for the ternary systems. A.E.S.

### Conduction of Heat in Oriented Polymers

V. A. Kargin, G. L. Slonimskii, and Yu. S. Lipatov  
*Doklady Akad. Nauk S.S.S.R.*, **104**, 96-97 (1 Sept. 1955)

Samples of polymethyl methacrylate (mol.wt.  $\sim 5 \times 10^5$ ) (I), polystyrene (mol.wt.  $\sim 7 \times 10^4$ ) (II), polyethylene (III), and 6-nylon (IV) are stretched under suitable conditions (I by 100% at 115°C., II by 1000% at 118°C., III and IV in the cold until necking is complete). A readily fusible film of a wax preparation is applied to one side of the sample, and a hot rod having a truncated conical end (area of tip 0.7 sq. mm.) is applied to the opposite side. The figures formed by the melting of the wax on the oriented amorphous polymers I and II are circular (conduction of heat is not anisotropic), whereas those formed on the crystalline polymers III and IV are elliptical (anisotropic conduction). It is thus shown that, although oriented amorphous polymers are anisotropic with respect to many properties (mechanical properties, thermal expansion, refraction of light) as a result of the anisotropic distribution of chemical bonds, they are not anisotropic with respect to thermal conductance. It is considered that the low restraint on thermal agitation in amorphous polymers results in heat-transfer effects that level out the effect of anisotropic structure. A.E.S.

### Polyacrylonitrile Fibres

#### IX—Polymerisation of Acrylonitrile in Inorganic Salt Solutions

A. Hunyar and V. Gröbe  
*Faserforsch. und Textiltech.*, **6**, 548-553 (Dec. 1955)

Polymerisation of acrylonitrile in salt solutions is examined and that in aqueous  $\text{ZnCl}_2$ - $\text{CaCl}_2$  solutions studied in more detail using  $\text{FeCl}_3$  and ultraviolet radiation for initiation. With this method polymerisation can be stopped at an appropriate moment and the resulting polymer solution can be spun to give fibres of good quality.

#### X—Dissolution of Copolymers of Acrylonitrile in Organic Solvents

A. Hunyar  
*Ibid.*, **7**, 13-17 (Jan. 1956)

Some copolymers of acrylonitrile are characterised by their solution temperatures in organic solvents. W.R.M.

### PATENTS

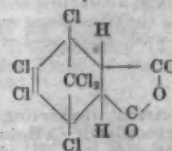
#### Stabilised Acid Natural Rubber Latex

Revertex  
Natural rubber latex is brought to pH 5-7 in presence of a non-ionic surface-active agent, e.g. Lissapol N (ICI), and then concentrated by evaporation or centrifuging. C.O.C.

#### Flame-resistant Ethoxyline Resins

General Electric Co. BP 744,388

The compound—



(obtained by a Diels-Alder condensation of maleic anhydride and hexachlorocyclopentadiene) is a curing catalyst for ethoxyline resins (polyether derivatives of polyhydric organic compounds containing epoxy groups) to which they also impart flame-resistant properties. C.O.C.



**Metal-coated Polyethylene Terephthalate Film**

DuP *BP 743,281*  
Polyethylene terephthalate film, e.g. 0.25 mil thick, is biaxially stretched at least 2.5 times its length and heat-set at 150° to 250°C. A metallic coating,  $\leq 0.0001$  mil, preferably 0.0004–0.0008 mil thick is applied by vacuum metallizing, electroplating, chemical reaction or electrostatic spraying. The metallized film is more highly resistant to water vapour and organic vapours, has an electrically conductive surface, and may be used for decorative purposes. K.W.

**Surface Colour and Relief Effects on Thermoplastic Sheet**

J. H. Bencke Hannover *BP 742,752*  
Dyed thermoplastic sheeting is printed with a pattern resembling a textile fabric or plaited work and is then embossed with a pattern reproducing the surface texture of such textile or plaited work. C.O.C.

**Imparting a Slip Finish to Vinyl Resin Sheeting**

United States Rubber Co. *USP 2,705,690*  
A slip finish is imparted to vinyl resin sheeting or vinyl resin coated fabric by coating it with a composition containing a polyethyl methacrylate, a polymethylmethacrylate, polyvinyl chloride or a vinyl chloride-vinyl acetate copolymer, and either a silicone fluid or a soluble silicone rubber. C.O.C.

**Oxygen-containing Groups on the Surface of Carbon Black (IV p. 181)**

Strain in Lactams (VI p. 185)

Patterned Mechanical Finish on Thermoplastic Sheets or Fabrics (X p. 194)

Coating Strip Material and Producing Foils (XI p. 197)

Tough, Flame-resistant, Dimensionally Stable, Heat-stable Cellulose Derivatives or Vinyl Resin Plastic Compositions (XI p. 197)

**XIV—ANALYSIS; TESTING; APPARATUS****Microdetermination of Primary Aromatic Amines by Potentiometric Titration with Sodium Nitrite**

L. M. Litvenenko and A. P. Grekov  
*J. Anal. Chem. U.S.S.R.*, 10, 164–168 (May–June 1955)  
The aromatic amine (0.01–0.05 millimole) is dissolved in 5–20 ml. of 2–10% HCl (if difficultly sol., the amine is first dissolved in acetic or formic acid, and aq. HCl is added to a concn. of 2–10%), and KBr (catalyst) is added to a concn. of 0.3–0.4 M. The soln. is stirred vigorously, and 0.01 M NaNO<sub>2</sub> is added from a microburette, the tip of which is below the level of the liquid. The changes in the potential of a Pt electrode immersed in the liquid are observed (a freshly prepared quinhydrone electrode in a soln. containing HCl (0.01 M) and KCl (0.09 M) is used as reference electrode), the end-point being indicated by a rapid change. Primary aromatic amines varying greatly in structure and basic character can be determined, accurately within 1%, with equal readiness. A.E.S.

**Instrumental Ranking of Fabric Handle. II—Relation between the Withdrawal Resistances of Fabrics through a Ring-hole and their Compressibilities**

H. Uchida, T. Takizawa, and M. Kobayashi  
*J. Soc. Textile Cellulose Ind. Japan*, 11, 808–812 (Dec. 1955)

**Determination of the Distribution of Fibres in Blended Yarns**

P. Kaasenbeck and J. A. Jacquemart  
*Bull. Inst. Text. France*, (57), 15–24 (Dec. 1955)  
A length of the yarn is wound helically on a Plexiglas rod in which is cut a thread of suitable pitch. The bobbin thus prepared is immersed in methyl methacrylate in a test-tube. After polymerising, the tube is broken away, and a section ( $< 100 \mu$ ) cut along the axis of the rod.

Such sections, containing a large number of cross-sections of the yarn, are examined microscopically, after dyeing if necessary. The method permits rapid statistical checking of blended yarns. J.C.F.

**Fluorescent Spots in Raw Cotton associated with the Growth of Micro-organisms**

P. B. Marsh, K. Bollenbacher, J. P. San Antonio, and G. V. Merola

*Text. Research J.*, 25, 1007–1016 (Dec. 1955)

Growth of certain fungi on cotton before harvest is shown to give rise to fluorescent spots when the raw cotton is examined in ultraviolet radiation. The test is not a general one for fungal infection present in commercial cotton. J.C.F.

**Refractometric Determination of the Fat Content of Raw Wool**

G. Nitschke  
*Faserforsch. und Textiltech.*, 6, 566–568 (Dec. 1955)

**pH Measurement of Wool Extracts**

H.-H. Bühler and H. Zahn  
*Textil-Praxis*, 11, 76–77 (Jan. 1956)

Measurement of the pH of wool extracts represents a valuable means of assessing wool qualities, and for accurate results the I.W.T.O. standard method is recommended. In many instances the requirements of industry can be met by the use of shortened methods. B.K.

**Penetration of Alkaline Solutions into Wool Fibres determined by Changes in the Modulus of Rigidity**

M. Karrholm, G. Nordhammar, and O. Friberg

*Text. Research J.*, 25, 922–929 (Nov. 1955)

An apparatus is described for the determination of torsional rigidity and rigidity modulus. Tests using wool fibres treated with either KOH in ethanol or NaOH in butanol-paraffin showed a 10% decrease in modulus of rigidity in the first case, but no change was observed in the second. The modulus of rigidity is said to be a more sensitive indication of changes in the outer parts of the fibre than Young's modulus. W.R.M.

**Measurement of the Double Refraction (Birefringence) of Artificial and Synthetic Fibres**

T. Zylinaki and J. Godek  
*Zeitz. Nauk. Politech. Lodz.*, No. 4 (Włókiennictwo 1), 21–48 (1954)

A comparison is made of known methods for the measurement of double refraction, and those of immersion and interference as applied to artificial and synthetic fibres are treated in detail. The work is illustrated by theoretical diagrams, photomicrographs of some of the specimens used, and tables of the results obtained. To facilitate the use of the interference or the compensating-colours method, a special sliding chart is devised and clearly explained. A very comprehensive analysis of the errors is made and the accuracy of the results is calculated. T.Z.W.

**Determination of the Whiteness of Fabrics with the FT-1 Textile Photometer**

L. I. Belen'kii, M. E. Kazanskaya, V. S. Khazanov, and S. G. Yurov

*Tekstil. prom.*, 15, 43–47 (April 1955)

The FT-1 textile photometer was devised for the accurate assessment of whiteness. Its optical and electrical systems are described and shown diagrammatically; an antimony-caesium vacuum photocell is used, and this receives light scattered at an angle of  $45 \pm 10^\circ$  from fabric illuminated perpendicularly. In the recommended method of measurement for practical purposes, "monochromatic" relative brightnesses ( $r$ ) are determined at 400–480 m $\mu$  ( $r_1$ ) and at 500–560 m $\mu$  ( $r_2$ ). The whiteness of a fabric is then described as e.g. 81.2 (0.95), indicating that  $r_1 = 81.2\%$  and  $r_1/r_2 = 0.95$ ; when  $r_1/r_2$  is less than unity the white is yellowish, and when  $r_1/r_2$  is greater than unity the white is bluish. The instrument will determine relative brightness accurately within  $\pm 0.1\%$ , and the whiteness results are reproducible within  $\pm 0.2\%$ . A.E.S.

### Iodine Sorption and Crystallinity of Cellulose Fibres. XI—Assessment of Linen Bleaching by Iodine Sorption

K. Schwortassek

*Faserforsch. und Textiltech.*, 6, 545-548 (Dec. 1955)  
Determination of the amount of amorphous material by iodine sorption is used as a means of evaluating degradation in a bleaching process. It is concluded that the method is a useful supplement to more usual ones. W.R.M.

### Effect of Temperature on Absorption of Iodine by Cellulose

A. G. Chitale

*Text. Research J.*, 25, 886-887 (Oct. 1955)  
The absorption of iodine is found to fall with increasing temperature, and it is suggested that, in determinations of accessibility, absorption by the sample and by a standard amorphous material should be determined at the same temperature. An equation is given for converting absorption at one temperature to that at another. W.R.M.

### Control of the Vat Dyeing Process

L. I. Bel'enkii and M. E. Kazanskaya

*Tekstil. prom.*, 14, 20-24 (Feb. 1954)  
*Amer. Dyestuff Rep.*, 45, 54-57 (30 Jan. 1956)

A set of laboratory control methods, characterised by the use of physicochemical apparatus, are described for studying the alkali, hydrosulphite, and dye (leuco, in suspension, and on fibre) concentrations in vat dyeing. Using parallel Pt electrodes it is shown that rapid changes in potential of alkaline ( $\text{Na}_2\text{CO}_3$ , pH 10-8) solutions of hydrosulphite occur in the first few minutes, after which an equilibrium value is slowly reached. Large differences in absolute values of oxidation-reduction potential are observed only with low hydrosulphite concentrations. Oxidation of the hydrosulphite, however, is characterised by a distinct change in potential. Similar phenomena are observed in solutions buffered at pH 7-1. Introduction of leuco dye solution markedly increases the potential; e.g. with Vat Blue R (0.3 g./litre) it is 960 mv. (Au electrode), compared with 880 mv. without the dye. The value of this potential or of the pH cannot be used to measure hydrosulphite concentration but can indicate the extent of reducing material in continuous processing. Of the large number of different ions present in a "working" solution  $\text{OH}^-$  ( $\text{NaOH}$ ) will conductometrically titrate first and accurately; a curve shows two breaks, the first corresponding to  $\text{NaOH}$ , and the second to all others, the presence of leuco compounds not interfering. Curves are illustrated and discussed. The concn. of leuco compound is determined by pipetting an aliquot into water containing  $\text{H}_2\text{O}_2$  and a protective colloid, e.g. ethylene oxide-dodecyl alcohol condensate, thus forming a highly dispersed pigment, which can be analysed in suspension photoelectrically. Parallel determination of dye on fibre is made by dissolving fabric in cold conc.  $\text{H}_2\text{SO}_4$ , diluting with water containing a protective colloid, and similarly measuring. Graphs are discussed. J.W.B.

### Level-off Degree of Polymerisation—Relation to Polyphase Structure of Cellulose Fibres

O. A. Battista, S. Coppick, J. A. Howsmon, F. F. Morehead, and W. A. Sisson

*Ind. Eng. Chem.*, 48, 333-335 (Feb. 1956)  
The level-off degree of polymerisation (D.P.) of hydrocellulose is related to crystallite particle length. Differences in the fine structure of cellulose fibres may be characterised by following the change in D.P. with progressively more severe swelling treatments. Lateral-order distributions obtained in this way agree with those obtained by independent methods such as moisture regain or formylation. Electron-microscope measurements of particle lengths of D.P. hydrocelluloses agree well with the average lengths calculated from intrinsic viscosity measurements in cuprammonium hydroxide. W.K.B.

### Colour Comparator for Determination of Water in Cellophane

H. A. Scopp and C. P. Evans

*Anal. Chem.*, 28, 143-144 (Jan. 1956)  
A light source furnishes two beams, one of which passes through the sample jar (titration vessel) and the other through a 670-m $\mu$  filter; both beams are viewed simultaneously on a ground-glass screen. The colour

produced in the course of a Karl Fischer titration of the sample (using Methylene Blue as indicator) is compared with that of the standard. A magnetic stirrer is used to agitate the sample, the methanol which extracts the water, and the titrating liquid. Several samples may be analysed in succession without changing the contents of the titrating vessel or removing the previous sample(s). In most cases the reproducibility is  $\pm 2\%$  or better, and this compares favourably with other methods. J.W.D.

### Comparison of Methods for Determining the pH of Chrome-tanned Leather

R. L. Sykes

*J. Soc. Leather Trades Chem.*, 40, 30-33 (Jan. 1956)

The apparent acidity of 100 chrome-tanned leathers has been determined by both the Atkin-Thompson and the American Leather Chemists' Association methods. Both methods give highly reproducible results, but do not agree with one another; there is, however, a very significant association between them. It is not possible, within reasonable limits of certainty, to predict the value given by one of these methods from a knowledge of that experimentally obtained by the other. The A.L.C.A. method is recommended in view of its simplicity. J.W.D.

### PATENT

#### Measuring the Colour of White Substances

D. W. Kent-Jones and A. J. Amos BP 746,074

Modification of BP 669,950 (J.S.D.C., 68, 236 (1952))

Light from a single source travels in two paths each containing both an infrared filter and a filter passing only light of 500-560 m $\mu$ . The light in one path is directed on to the surface to be measured, whence it is reflected through an optical system including an adjustable shutter. The amount of light at the end of each path is measured by a pair of photoelectric cells in circuit with an electric current-measuring instrument responsive to the difference in the photoelectric currents. The shutter is adjusted so that a null or datum reading is obtained for the electric current, the amount of adjustment of the shutter being compared with that obtained when a standard white surface is used. C.O.C.

#### Condensed Phosphates (III p. 174)

2:2'-Diaminodiphenyl and 2- and 4-Aminodiphenylamine in the Products of Benzidine Rearrangement (IV p. 178)

Stress Relaxation of Fibres as a Means of Interpreting Physical and Chemical Structure. I—Determination of Relative Accessibility (VI p. 184)

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Dissolution of Copolymers of Acrylonitrile in Organic Solvents (XIII p. 198)

## XV—MISCELLANEOUS

### Colour Certification

Anon.

*Federal Register*, 20, 8492-8495 (16 Nov. 1955)  
*Chem. Abs.*, 50, 1222 (25 Jan. 1956)

FD&C Orange No. 1 (mono-Na salt of 4-p-sulphophenylazo-1-naphthol), FD&C Orange No. 2 (1-o-tolylazo-2-naphthol), and FD&C Red No. 32 (1-xylylazo-2-naphthol) are no longer permitted to be used in the U.S.A. for food but may be used in drugs and cosmetics. C.O.C.

### PATENT

#### Coating with Silver

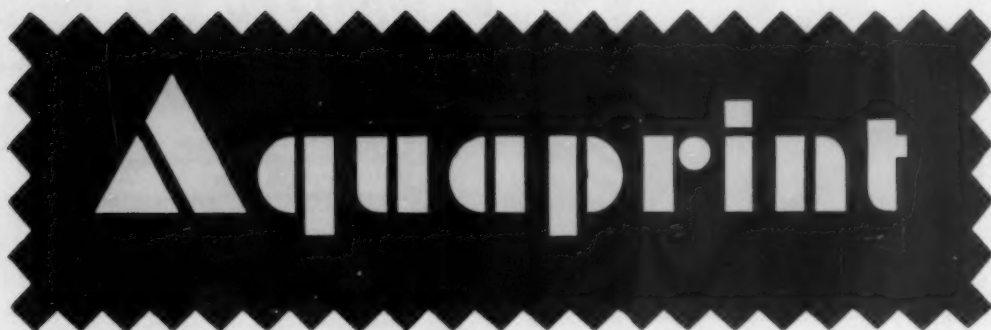
Philips Electrical Industries

BP 745,857

The articles are brought into contact with solid silver lactate or butyrate at  $> 150^\circ\text{C}$ , so as to melt the silver salt and yield a coating which decomposes to silver. To ensure complete decomposition to silver the coating may be heated for some time after it has been applied. C.O.C.

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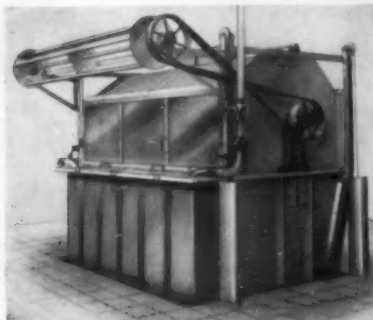
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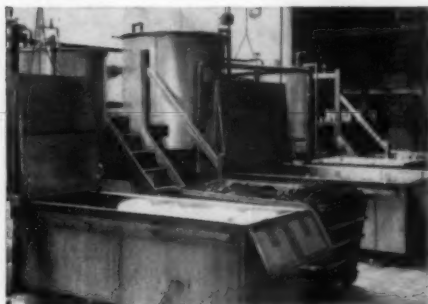
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 Grunberg, A. W., formerly of 69 Mantion Street, Fall River, Massachusetts, U.S.A., to Carrera 17, No. 32-18, Bogota, Columbia, S.A.  
 Holmebakk, G. A., formerly of 120 Lewis Road, Droylsden, Manchester, to 27 Canterbury Street, Ashton-under-Lyne, Lancs.  
 Kubba, S. M., formerly of 63 Haypark Avenue, Belfast, to 10 Malone Road, Belfast, N. Ireland  
 Levi, S. S., formerly of Dept. of Comm. & Industries, Dye Chemists Lab., Aba, Nigeria, to Federal Dept. of Commerce and Industries, Lagos, Nigeria, B.W.A.  
 Lomas, J., formerly of Heathfield, Birch Vale, near Stockport, to 81 Moss Bank, Crumpsall, Manchester 8  
 Mackin, J. F., formerly of 3 Milliken Place, Milliken Park, Kilbarchan, to "Darnaway", Armour Place, Johnstone, Renfrewshire  
 Nunes, L. F. M., formerly of R. Conselheiro, S. Veigas, 73 Covilha, Portugal, to Rua Actore Vale, 30-4 Frente C., Lisbon, Portugal  
 Pollard, W. S., formerly of Shelling Hill, Cullybackey, N. Ireland, to "Isafield", Drymen Road, Balloch, Dunbartonshire, Scotland  
 Rakosi, Dr. T., formerly of Kurdaneh Textile Works Ltd., P.O. Box 3045, Haifa, to Singer Str. 10, Kiriat Bialik, Israel  
 Reed, F. G., formerly of 353 St. Patrick West, Magog, P.Q., Canada, to 108 Victoria Street, Magog, P.Q., Canada  
 Slater, W. K., formerly of 24 Milverton Road, Whitecraigs, Renfrewshire, to 85 Hope Road, Sale, Cheshire  
 Tebb Pitt, R. H., formerly of H. H. York & Co. Pty. Ltd., 573 Lonadale Street, Melbourne C.1, to 76 Ardroyne Street, Black Rock, Melbourne S.9, Australia  
 Tinsedall, C. D., formerly of Bangalore Woollen, Cotton & Silk Mills Co. Ltd., Bangalore 2, India, to Buckingham & Carnatic Mills Ltd., Perambur Barracks P.O., Madras-12, India  
 Walz, G. F., formerly of United States Fin. Co., Norwich, Conn., to USF-Aspinook Fin. Division, Gers Corporation, Norwich Plant, Norwich, Conn.  
 Wills, C., formerly of The Yates Bleachery, Flintstone, Georgia, U.S.A., to 1508 St. Paul Street, Three Rivers, P.Q., Canada  
 Wilson, G., formerly of 2 North Royd, Hipperholme, Halifax, to 198 Rochdale Road, Halifax, Yorks.  
 Young, D., formerly of 33 Fairfield Road, Toller Lane, Bradford 8, to 66 St. Mary's Road, Heaton, Bradford

## SITUATIONS VACANT AND WANTED etc

The Publications Committee is prepared to receive Advertisements relating to SITUATIONS VACANT, SITUATIONS WANTED, or MISCELLANEOUS ITEMS for insertion on this page of the Journal. Advertisements of Situations Wanted are gratis to individual members, but must not exceed twenty-four words in length.

All inquiries relating to Advertisements in the Journal should be addressed to THE GENERAL SECRETARY, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE.

Replies may be addressed Box —, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE, where all communications relating to these Advertisements are treated in strict confidence.

### SITUATIONS VACANT

The engagement of persons answering these advertisements must be made through a Local Office of the Ministry of Labour or a Scheduled Employment Agency if the applicant is a man aged 18-64 inclusive or a woman aged 18-59 inclusive unless he or she, or the employment, is exempted from the provisions of the Notification of Vacancies Order 1952

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Apply in writing to Box V98 giving full particulars of education, experience, interests, also attach a photograph.

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## JOURNALS WANTED

The Society is urgently wanting copies of the January and February 1956 issues of the Journal and the General Secretary would welcome the opportunity of acquiring copies for these months

### ADDRESSES WANTED

Bromby, N. G., formerly of 170 Palatine Road, West Didsbury, Manchester  
Coles, G. H., formerly of c/o Messrs. S. Hubbard Ltd., Regent Mill, Luton  
Crook, B., formerly of 196 Wentworth Street, W. Magog, Quebec  
Crowther, D., formerly of 551 Leeds Road, Thackley, Bradford  
Desmond, J. J., formerly of 1416 Molcomb Road, Huntingdon Valley, Pa., U.S.A.  
Drzewidki, M., formerly of 3 Ruskin Drive, Morecambe  
Faulkner, J., formerly of 31 Circular Road, Ballymena, County Antrim, Northern Ireland  
Harvey, H. C., formerly of 77 Edinburgh Road, Congleton, Cheshire  
Hatton, C. A., formerly of 206 Blackpool Road, Lea, near Preston

Helliwell, G. S., formerly of 12 Stoneygate Road, Leicester  
Kesprek, A. E., formerly of 15 Huntley Street, Hamilton Street, Ontario, Canada  
Kupczyk, J., formerly of 5 Rutland Grove, Farnworth, Lancs.  
Meier, P. W., formerly of Oberwilerstrasse 38, Basle, Switzerland  
Moore, G., formerly of 30 Welwyn Avenue, Wrose, Shipley  
Stamires, D., formerly of 9 Shaw Lane, Leeds 6  
Villiers, R. F., formerly of Kingecote, Locker Lane, Hynes Road, Lancaster  
a Visconsa, G. I. S., formerly of Dvozione Centrale degli Etabiliment (Dott. Calandra), Via Sicilia 102, Roma, Italy  
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